FUNDAMENTALS OF CHEMISTRY AND APPLICATIONS

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FUNDAMENTALS OF CHEMISTRY AND APPLICATIONS

Chosen from Inorganic, Organic, and Biochemistry, with Applications in Everyday Concerns and in the Applied Sciences, Including Physiology, Cookery, Bacteriology, and Materia Medica

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PREFACE TO FIRST EDITION

This book has been written as the result of numerous requests made by many people during a period of years. It is intended for use in connection with a brief course in chemistry for the purpose of helping to make more meaningful applied sciences and arts such as physiology, cookery and nutrition, bacteriology, materia medica, and nursing practice.

The usual one year course in high school chemistry and the usual first year course in college — the former an abbreviated replica of the latter — are devoted almost exclusively to inorganic chemistry and are chiefly designed to prepare students for further study of chemistry in the traditional manner — high school students for chemistry in college, college students for further courses in chemistry. And, naturally, text books for these courses are patterned accordingly. This scheme serves admirably for students who are to become chemists in one line or another, but it does not serve at all well for the multitude of other students.

Among the latter are those whose curricula requirements in certain specialized schools, including all schools of nursing and some schools in home economics, call for a half year of chemistry — or at most one year — as a service course for the applied sciences and arts mentioned above. A course planned for such purpose should include content selected not only from inorganic chemistry but from organic and biochemistry as well; but since each of these fields is extensive in itself it follows that for such an abbreviated and inclusive course the content selection must be highly limited and carefully made, and the manner of treatment should be consistent with the purpose.

It is for such a course in chemistry and with these intents continuously in mind that this book has been written.

The general plan and the content selection are much the same as are recommended for a course in chemistry in the Curriculum Guide for Schools of Nursing of recent publication.*

Somewhat more than one half of the book is devoted to the presentation of fundamentals which of necessity must comprise a part of any first course in chemistry, but the manner of presentation is more detailed than is usual with chemistry texts for the reason that the more condensed the chemistry course, the greater must be the proportion of assistance provided for the students either by teacher or text; and teachers in such schools as have

* Curriculum Guide for Schools of Nursing, National League of Nursing Education, 1937.

been mentioned are quite commonly overburdened with a number of subjects and many hours of teaching load.

Other features of this text are as follows. Oxygen is the only simple substance that is studied in detail and the chief emphasis is centered around the fact that its vital physiological use and its use in man's external concerns is due to its being a reservoir of an enormous amount of energy. One chapter is devoted solely to energy transformations that accompany matter transformations in many chemical reactions. More than the usual amount of emphasis is given to the study of water as to its physical and chemical properties and the bearing of these properties on the affairs of man.

The text material involving molecular weights and atomic weights as unit weights for measurable quantities of substances and elements, also molecules and atoms as theoretical ultimates of substances and elements, is presented in greater detail than is customary. Valences of atomic weights versus valences of atoms are treated in like detail. Many students confuse these issues and adequate help is not usually provided in text books for clarifying these concepts. The use of symbols and formulas as abbreviations for the written names for elements and substances is discouraged, likewise the use of the formula equation as a convenient substitute for the word equation. It is through such practices on the part of beginning students in chemistry that these shorthand devices lose their quantitative significance.

Included in the chapter with solution is more material appertaining to colloidal solutions and emulsions than is likely to appear in beginning texts on chemistry. This has seemed necessary because some information in regard to the properties of colloidal solutions in comparison with those of true solutions has become essential to the better understanding of many phenomena with which applied sciences are concerned.

The theory of partial ionization on the part of electrolytes originally conceived by Arrhenius is presented rather than the Debye-Huckel theory of complete ionization, since the former provides all that is necessary for the sort of course for which this text is intended. Special attention is given to water as an ultra-poor electrolyte and to the concentration relationship that must be met on the part of hydrogen ions and hydroxyl ions when water as an electrolyte attains equilibrium. This emphasis is due chiefly to the increasing tendency in the applied sciences to present these concentrations quantitatively in terms of cH and cOH, or in terms of their power pH and pOH notations, as factors to be

reckoned with in various phenomena. The discussion of this quantitative relationship has been carried only as far as the negative-power-of-ten values, no attempt having been made to deal with the reciprocal relationships. Neither the mathematical equipment of most students of beginning chemistry nor the scope of this text would seem to justify this latter step.

The organic chemistry and biochemistry are integrated, the chief purpose of the organic chemistry being that of providing service information for the better understanding of carbohydrates, fats, and proteins, the digestive reactions and such metabolic reactions as are discussed. Portions of the chapter on cyclics and derivatives are developed with the intent of placing especial emphasis on the theoretical accounting for similarities and differences among members of some classes of drugs.

The final chapter on the physiological functioning of salts deals with such studies as reactions through which salts aid indirectly in obtaining optimum hydrogen ion concentrations for digestive reactions, and in maintaining the hydrogen ion-hydroxide ion concentration relationship within the blood, lymph, and cells within the exceedingly limited normal range. It deals, too, with reactions involving salts which are contributing mechanisms toward effecting carbon dioxide and oxygen exchange in reverse manner at the lungs and cells.

This book is not intended as a substitute for an inorganic text, an organic text, or a biochemistry text. Students who seek something more comprehensive in these lines must look to other courses and other texts. It is intended, as has been repeatedly stated, for students who are chiefly interested in applied sciences and arts and who wish to have but one brief course in chemistry for the purpose of making these studies somewhat more meaningful. The entire content of this text and the manner of treatment of this content have been selected and shaped toward such end. However, while patterned for specific groups of students, the thought does persist that the type of chemistry course which this text aims to serve may, after all, be the type of course that, with some elaborations, really should be given as a first course in undergraduate college chemistry and in a modified form in the high school.

Our profound gratitude goes out to many students of many years whose manifold expressions of appreciation have been chiefly responsible for our yielding to persuasions to attempt to put some of our ideas between the covers of a book.

THE AUTHORS

May, 1939

PREFACE TO SECOND EDITION

The purpose of this text and considerations as to selection and treatment of content are the same as discussed in the foregoing preface to the first edition. Outstanding changes are as follows:

The chapter dealing with molecular weights and molecules, atomic weights and atoms, valences, and short-hand practices in respect to these chemical measurings have been considerably simplified.

For convenience in reference a table of valences is given on the back fly leaf of the text.

While the content of the chapter on true and colloidal solutions and emulsions is the same as in the first edition of the text, it has been reorganized in such a way that assignments for student study in briefer courses can be more effectively made. However, it should be emphasized that considerable portions of this chapter have always been and continue to be intended chiefly for reference and as a help toward providing answers for various questions such as students during many years have been bringing to the authors from courses other than chemistry — chiefly physiology, materia medica and nursing practice.

The subject of ionization has been revised to conform with the more modern theory of complete ionization as to strong electrolytes.

The chapter on cyclic compounds has been reorganized and completely revised. Material on chemotherapy has been introduced in recognition of the increasing importance of this aspect of therapeutic treatment.

Instead of a separate chapter on the vitamins they are dealt with at different points in the text either from the standpoint of their chemical composition in relation to the composition of other compounds under discussion or from the standpoint of their proven relationship to physiological processes under discussion. The authors are of the opinion that more detailed treatment as to vitamins is a function of biochemistry and nutrition; not of an already overcrowded course in the fundamentals of chemistry.

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March, 1943

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CHAPTER I

Substances and How They Are Recognized. Mixtures

Substances. *A chemical change can be defined as a change during which a given substance or substances go out of existence as a new substance or substances are made.* Substances, then, are of prime consideration in chemical acts. As a consequence, in order to clear the way for an understanding of chemical reactions, it is first essential to have a clear notion of what constitutes a substance and how to recognize the same. Unfortunately for our purposes this word *substance* is used variously; a dictionary, indeed, may present half a page of different meanings, whereas our need is in respect to one very specific meaning and one only.

For example: after one meaning, sugar solution can quite properly be called a substance but from the standpoint of our usage sugar solution is not a substance but is made up of two substances. The liquid part evaporates because it is water and all specimens of water are liquid, at ordinary temperatures, and volatile. The solution is sweet, and equally sweet in all parts, because of the cane sugar present therein, since cane sugar is sweet and soluble in water, hence distributes evenly throughout the same. Thus we are pointing at the *water* and calling it *a substance* and at the *cane sugar* and calling it *a substance* because each has its own set of properties.

And again, after one meaning, steel is a substance; but from another standpoint steel is at least two substances. The iron component is gray, shiny, magnetic, and subject to rusting because these properties are characteristic of iron; but iron is also soft, therefore, the hardness of steel must be due to the presence of another substance, and frequently this substance is chromium which, like iron, is gray and shiny but, unlike iron, is hard, nonmagnetic, and

not subject to rusting. So we are pointing at *iron*[1] and at *chromium*[1] and calling *each a substance because it has its own specific properties.*

Naturally these four substances have other properties, some of which, including those already specified, are as follows:

Water	*Cane sugar*	*Iron* (*substance*)	*Chromium* (*substance*)
colorless	colorless	gray	gray
odorless	odorless	solid	solid
tasteless	sweet	soft	hard
liquid	solid	magnetic	nonmagnetic
volatile	soluble in water	rusts	not subject to rusting
solvent for many substances	less soluble in alcohol		
not solvent for some substances			

Furthermore, within whatever matter specimens these substances may be they exhibit their own respective properties. Accordingly, the water component of any spring or pond, of blood, of the sap of a plant, or of milk exhibits the above properties, as well as other properties that have not yet been considered. The cane sugar component of cake or of the sap of sugar cane is colorless, odorless, sweet, and soluble. And in the same manner the iron component of any steel or of any cast iron exhibits its own properties.

In general, then, the word *substance* in this text will be applied to a *material all specimens of which exhibit the same set of properties.* It follows, therefore, that, should there be two sets of properties in respect to a given material, then two substances are present; should there be three sets of properties as to a given material, then three substances are present; etc.

According to such specifications, copper,[2] carbon,[2] grain alcohol, sodium chloride, iron rust, and sulfur[2] are also substances because each is material and each presents a definite set of properties. Hence:

Copper (*substance*)	*Carbon* (*substance*)	*Grain alcohol*
solid (at ordinary temp.)	black	liquid (at ordinary temp.)
reddish brown	solid	volatile
good conductor of heat	insoluble in water	colorless
good conductor of electricity	burns with oxygen	has a characteristic odor
nonmagnetic		has a characteristic taste
subject to tarnishing		burns with oxygen
		has a characteristic physiological effect

[1] The words *iron* and *chromium* are used both for the *substances* and the *building materials* (p. 14).

[2] See fine print p. 14.

As a reasonable outcome of this individuality of substances it becomes evident that the *means for the recognition of the presence of a substance must be by way of its properties.* For example: wherever *copper* may be, whether alone or mixed with other substances as in copper dishes or wire, its presence is recognized by its telltale reddish brown color; and copper has other properties, but this is the one most easily observed. The same holds as to *grain alcohol* because, whether mixed only with water or with many other substances as in alcoholic beverages or "working fruits," one can tell that the grain alcohol is present because of its revealing odor and taste.

Properties of substances. Inasmuch as properties are the all important means whereby substances make themselves manifest, a summary view of the same and a sorting out of such as are commonly considered should be in order.

Thus, in general, there are some properties such as *color, odor,* and *taste* which are more or less easily ascertained and which should receive consideration when they apply conspicuously to the substance under scrutiny. But, although *helpful* toward the ultimate recognition of a substance, these properties are not identifying. For example: to find that a given substance is white, solid, and odorless constitutes three helpful steps toward discovering what it is; but these properties are *not identifying* because many substances — starch, sugar, and sodium bicarbonate among them — are white, solid, and odorless. Again, to note that a substance under investigation is solid, gray, and malleable is decidedly helpful toward finding out what the substance is; but more data are needed for actual identification because a number of substances — as for example: silver, nickel, and aluminum — have this selection of properties.

Some significant but not identifying physical properties

Color
Odor
Taste
Physical state — solid, liquid, gas
Solubilities — in water or other specified solvent
$\left.\begin{array}{l}\text{Crystalline or not}\\ \text{Hardness}\\ \text{Malleability}\\ \text{Ductility}\end{array}\right\}$ if solid
Volatility — if liquid

But there are other properties of a substance, such as *density, boiling point,* and *freezing point,* which, although skilled technic is required for their determination, absolutely *identify* the substance when said properties are obtained correctly. The definitions that make these properties identifying are as follows:

Density: the weight of a given volume of a substance at a given temperature and, if gaseous, under a given pressure.

Boiling point (B.P.): the temperature at which the pressure of the vapor leaving a substance in the liquid state is equal to the pressure exerted by a column of mercury 760 mm. high (called standard pressure).

Freezing point (F.P.): the temperature at which the *solid* and *liquid* phases of a substance can *persist in the presence of each other without change in temperature* on the part of either phase.

For example: 1 cc. of water at 4° C. weighs exactly 1 gram. This constitutes one density figure for water, and 1 cc. of no other substance in existence at this given temperature has this exact weight.

Again, when solid water (ice) at any temperature below 0° C. and liquid water at any temperature above 0° C. are mixed their temperatures will change, that of the ice will rise (without melting), that of the liquid water will lower, *until 0° C. is reached.* From then on, both the solid water and liquid water will remain continuously at 0° C. as long as both phases are in contact; then, if the environment outside is warmer the ice will melt gradually but will remain at 0° C.; if the environment is colder the liquid water will gradually freeze but will remain likewise at 0° C., with no temperature change possible until the water is either all liquid or all solid. This is what makes 0° C. the freezing point of water; and it is an identifying property, since the solid and liquid phases of no other substance than water can remain continuously in contact with each other with both phases remaining at 0° C.

And yet again, always when the temperature of water, if pure, reaches 100° C., the pressure of the vapor leaving said water is equal to the pressure exerted by a column of mercury 760 mm. high; hence the boiling point of water is 100° C., and no other substance in existence has exactly this boiling point, because the vapor of no other substance attains this pressure at this temperature.

And here is another example of the functioning of these properties: the temperature at which the solid and liquid phases of grain alcohol remain continuously in the presence of each other without either phase undergoing a temperature change is − 117.3° C.; hence this is the freezing point (or melting point) for grain alcohol and for this substance only. 78.5° C. is the temperature at which the pressure of grain alcohol vapor leaving the surface of this substance in the liquid state (if pure) is equal to the pressure exerted by a column of mercury 760 mm. high (or standard pressure); hence 78.5° C. is the boiling point of grain alcohol, and no other substance has exactly this boiling point.

The following is a listing of these identifying properties for water and grain alcohol which have been discussed, also for the substances copper and iron:

Water	*Grain alcohol*	*Copper*	*Iron*
1 cc. at 4° C. weighs 1 gram	1 cc. at 20° C. weighs .789 gram	1 cc. at 20° C. weighs 8.9 grams	1 cc. at 20° C. weighs 7.86 grams
Freezing point is 0° C.	Freezing point is − 117.3° C.	Freezing point is 1083° C.	Freezing point is 1530° C.
Boiling point is 100° C.	Boiling point is 78.5° C.	Boiling point is 2310° C.	Boiling point is 2735° C.

Needless to say these properties can become meaningful for the student only through practice in telling what they signify on the part of the substances concerned.

Warnings. *Density* should not be confused with *specific gravity,* which refers to the *relationship between densities* of given sustances (p. 3).

The foregoing definitions for freezing point and boiling point should not be confused with the other and more usual ones given; namely, *freezing point as the temperature at which a liquid freezes; boiling point as the temperature at which a liquid boils.* These are correct definitions according to one usage, but they make boiling point and freezing point of a substance *variables,* whereas the definitions stressed here (p. 4) make boiling point and freezing point *fixed* values for a substance, hence the identifying properties claimed.

Unfortunately, students are inclined to regard these properties as "dry-as-dust" items. They are far from that, although little can be done for the nonthinking student to dispel this notion. However, certain it is that each boiling point, each freezing point, and each density that is determined *correctly* comes as the result of months or years of repeated laboratory investigations by skilled workers under carefully controlled conditions; and whenever such a value is obtained it is a scientific achievement and constitutes a great gift to physicists, chemists, and engineers. Therefore, a table of boiling points, or of freezing points, or of densities represents as many great achievements and as many great gifts to science as there are boiling points, freezing points, or densities for the substances concerned that are given therein.

There are other properties of substances that might be considered, such as whether or not they are volatile, elastic, or magnetic, but it is not necessary to exhaust the list of possible properties in this study. Suffice it to say that such properties as have not been mentioned can be brought into the picture when there is need for them.

Physical and chemical properties. Properties of a substance can be classified from the standpoint of whether in exhibiting the same the substance does not or does cease to exist.

Physical properties. Most of the properties already stressed are of the first variety and are called physical properties. The color of a substance, its odor and taste, its physical state, whether or not the substance is malleable or ductile, its boiling point and

freezing point are *physical properties of the substance because in exhibiting them the substance does not go out of existence.*

Chemical properties. But a substance possesses another variety of properties, called *chemical properties, in the exhibition of which the substance does go out of existence.* For example: the substance copper "tarnishes," but in doing so, that portion of the copper which has been thus affected yields up its existence to help make the familiar greenish substance that is known as copper tarnish. Consequently, the fact that copper tarnishes is one of its chemical properties. By similar reasonings, the specific rustings, corrodings, tarnishings, or burnings of other substances are chemical properties of said substances. Thus, iron rusts and silver tarnishes, but the portions of the substances iron and silver that have rusted or tarnished go out of existence during the reactions designated; the ability of iron to rust and of silver to tarnish are, accordingly, chemical properties of these substances respectively.

Other examples, more briefly summarized, are as follows:

Sulfur*, the substance*

<table>
<tr><td>solid (at ordinary temperatures)
yellow
odorless
insoluble in water
soluble in carbon bisulfide</td><td>These are physical properties of sulfur because in exhibiting them sulfur, the substance, does not go out of existence.</td></tr>
<tr><td>it burns with oxygen
it burns with iron</td><td>These are chemical properties of sulfur because in exhibiting them sulfur, the substance, ceases to exist.</td></tr>
</table>

Cane sugar

<table>
<tr><td>solid
white
crystalline
soluble in water
soluble in alcohol
sweet</td><td>These are physical properties of cane sugar because in exhibiting them this substance does not go out of existence.</td></tr>
<tr><td>it chars at a high temperature
it reacts with water to make glucose and fructose</td><td>These are chemical properties because in charring and in reacting with water cane sugar goes out of existence.</td></tr>
</table>

More, much more, in regard to physical and chemical properties of substances will be considered as we become acquainted with more and more substances.

Law of component substances. The chemist has learned that *any matter specimen must be composed either of only one substance throughout its mass or of two or more substances,* a fact which constitutes one of the fundamental laws of chemistry and which has come to be called the *Law of Component Substances.*

Perhaps to the student this seems a self-evident fact, but it is nonetheless a fact of which the experimenter must be continuously mindful; when he forgets it, conclusions in regard to happenings in beakers and test tubes are quite likely to go astray. The trouble is that matter specimens are not always as they seem to be to the eye. Sometimes a specimen, such as granite, gives obvious evidence of the presence of two or more substances. Many times, however, a specimen, such as a spoonful of sugar or a glass of water, may seem every particle of it to be the same substance when actually other substances than the known one really are present. It is because of the frequent occurrence of such a deceptive matter specimen that the careful experimenter, continuously mindful of the law of component substances, becomes cautious about attributing all observed reactions to the substance of his interest in the specimen under study. Hence he holds in reservation the possibility that an observed reaction may, after all, be due to another substance which, hidden and not in predominance, may nonetheless be there.

Many a laboratory reagent is material of this order, that is, as far as appearance goes, it looks as if every particle throughout were of the same substance, although, actually, traces of other substances, which the manufacturer has found it impossible to remove, are present. What these substances may be is usually not known and they are commonly called "impurities": meaning other substances than the one desired. Obviously the presence of such undesired and unknown substances is frequently a nuisance, in that they become responsible for troublesome reaction outcroppings which confuse observations in respect to the behavior of the known substance under study. It is for this reason that, many times, when the student is investigating the chemical behavior of a substance and is attracted by an irrelevant happening, the laboratory instructor will say: "Ignore that, it is due to an impurity," and will then proceed to direct attention to the phenomena that are significant.

Matter specimens which are composed of one substance throughout are exceedingly rare, if indeed such have ever been obtained. A sample of sodium chloride or a lump of copper, every particle of which is of the substance sodium chloride or of the substance copper, would be such a specimen. The term "pure" used in reference to matter in the most significant sense of the word would be in connection with such specimens as these.

A specimen of pure gold, then, would have particles of no other substance than gold anywhere within its mass; one of pure alcohol would, every least last particle of it, be just alcohol. But probably no specimen of pure sodium

chloride, or of pure copper, or of pure gold or alcohol has ever yet been obtained. Actually, matter specimens which get labeled "pure" are not pure in this sense but are specimens in which the mentioned substance may constitute ninety-five per cent or more of the total matter present.

Mixtures. A *mixture is material which is composed of two or more substances, and every substance present in a mixture is unaffected by the proximity of the other substances* in that it exhibits its own properties in the same manner as if it were present all by itself. Thus, in a mixture of cane sugar and starch, the cane sugar is sweet and soluble in water despite the presence of the starch, while the starch is tasteless and insoluble despite the presence of the sugar. In steel mixture the iron is magnetic and subject to rusting regardless of the presence of chromium or other substances. The oxygen of air mixture becomes a party to burning with carbon and with many other substances despite its mixed association with nitrogen and carbon dioxide.

The name, therefore, that has come to be applied to substances that contribute to a mixture, also the one suggested in the statement of the related law, is *components:* meaning, placed together without loss of individuality. Cane sugar and starch, then, are components of the first mixture mentioned above; iron is a component of steel and of cast iron; and oxygen is a component of air mixture.

Now mixtures have to be reckoned with all the time by chemists, by manufacturers, and by people in general. Nature throws substances together in mixture either in helter-skelter manner as in earth's crust, or else in more ordered manner as in plants and animals. Consequently, when the chemist or the manufacturer goes to nature for a substance — for gold or for sodium chloride from earth's crust, or for sucrose from an appropriate plant, or for lactose from milk — he finds it in a mixture with a few or many other substances. Also in the making of a substance in the laboratory or in the manufacturing plant — such as iron, or baking soda, or any acid, base, or salt — some other substance or substances get made along with it.

Separation of a substance from a mixture. As a result of this prevalence of mixtures, chemists and manufacturers have been obliged to devise means for the separation of substances of their interest from their mixed associates; and it is evident that the separation means should preferably involve procedures during the operation of which the desired substances do not go out of existence; in other words, it is preferred that the procedures should be

physical in nature. The following are some separation procedures of this order.

Evaporation can be used when one substance is easily subject to evaporation but not so the other component substances. Sugar can be separated from water after this method, also iodine from alcohol.

Solution, filtration, and evaporation, used successively, serve this end when one component substance is soluble in some selected solvent while the associated substances are not thus soluble. Sugar can be separated from sand after this method, with water as the solvent. Fat can be separated thus from meat mixtures, with ether used as the solvent.

Distillation can be employed for the separation of two or more liquid substances by taking advantage of their differing boiling points, hence of their differing temperatures of maximum volatility. Alcohol and water can be separated through such means.

Melting and draining can be used when the desired substance within the mixture has an easily obtained melting point, but not so as to the other substances present. After this manner sulfur is easily separated from other substances with which it is found mixed in the crust of the earth.

All of *these separation procedures are physical* in nature. The sugar and iodine remain sugar and iodine as the water and the alcohol are respectively separated from them by evaporation; the fat continues to be fat all during the solution, filtration, and evaporation used in effecting its separation from meat; the alcohol and the water never cease to be themselves during the vaporization and condensation involved in their separation by distillation; the sulfur remains sulfur as it melts and drains away from other substances.

Many times the separation of a desired substance from all save a very small percentage of other substances, with which it was originally in mixture, is a problem that taxes the ingenuity of the most capable and careful operators.

Questions

1. Sodium chloride, the major component of table salt, is a substance. Give reason. Why is ether a substance? Why is carbon (component of coal) a substance?

2. Silver is a white, solid substance capable of a high polish; it can be hammered into various shapes and can be drawn out into a fine wire; upon contact with egg it tarnishes; it has a melting-point of 955° C.; and 1 cc. of silver at 20° C. weighs 10.5 grams.
   a. Which of these properties are physical and why?
   b. Which, if any, are chemical properties of silver and why?
   c. Which, if any, are identifying properties and why?

3. Why are density values for water possible other than that given on p. 5?
4. a. Why is $-116.2°$ C. the freezing point of ether?
   b. Why is $34.5°$ C. the boiling point of this substance?
   c. Why are these identifying properties of ether?
5. What are the characteristics by which a mixture is recognized? Classify the following as to whether they are substances or mixtures and in each instance provide convincing evidence to support your claim: granite, sodium bicarbonate, air, milk, mercury, baking powder.
6. How would you proceed to separate alcohol from an alcohol-water mixture? Salt from a sand-salt mixture? Fat from meat mixture?
7. State the law of component substances.

CHAPTER II

Physical and Chemical Change

Substances can undergo changes which are physical and changes which are chemical in nature. Our chief interest will be with changes of the latter variety; but since it is impossible to obtain a complete understanding of chemical change without an understanding also of physical change we shall proceed first to the following study.

PHYSICAL CHANGE

When a substance undergoes a change during which it does not cease to exist said change is physical in nature. With this statement as to what constitutes a physical change in mind, let us put to a test the ability to recognize this type of change through a study of some matter changes of more or less common occurrence, such as moulding a lump of clay into a vase, freezing of water, vaporization of alcohol, and rusting of iron. In so doing we must keep in mind that the way to discover whether a substance is or is not there lies through its properties:

Moulding a lump of clay. *Before the change,* the substance is gray, solid, and smooth; *during the moulding* and when it is complete, the substance continues to be gray, solid, and smooth. Conclusion: the same set of properties is continuously in evidence during the change, hence the same substance is present in the vase as was previously present in the lump of clay; therefore, the *change in shape of the substance is a physical change.*

Freezing of water. *Before freezing,* the substance is colorless, odorless, tasteless, liquid, and nonburnable; *during and after freezing,* the substance concerned, although solid, is still colorless, odorless, tasteless, and nonburnable. Conclusion: four of the properties are the same and these serve as evidence that the same substance is involved before, during, and after the freezing; therefore, it is reasonable to conclude that when water *freezes* it undergoes *a physical change.*

Vaporizing alcohol. The substance *before the change* is colorless, liquid, and has a pleasant, characteristic odor; *during vaporization,* the substance, although gaseous, is colorless and has the same characteristic, pleasant odor. Conclusion: the same odor provides evidence that the liquid substance and the gaseous substance are the same, hence the *change* involved *is physical* in nature.

Rusting of iron. *Before the rusting,* the substance is gray, solid, tenacious, and magnetic; *during the rusting,* there appears a substance which is reddish

brown, solid, crumbly, and nonmagnetic. Conclusion: since iron rust has a different set of properties than those of iron, they must be different substances, hence *the change* involved when iron rusts is *not physical in nature.*

Thus, as these reasonings signify, all but one of the foregoing changes on the part of the substances concerned are found to be physical in nature. Furthermore these are typical of many physical changes which we encounter daily: change in shape, as in mouldings and bendings; change in size of pieces, as in cuttings and grindings; change in physical state, as in melting, vaporization, and the reverse; change in temperature of the substance, from hotter to colder, and vice versa; distribution of one substance throughout another, as in mixing and dissolving. And let it be emphasized again, that these are physical changes, because, throughout said changes, the substances participating continue to be the same substances as evidenced by the presence of significant properties by which they can be recognized.

CHEMICAL CHANGE

When a substance undergoes a change as a result of which it ceases to exist and another substance or substances are made, the change is chemical in nature. The evidence of such a change is obvious: if a substance is gone its properties disappear along with it; vice versa, as another substance is made, its presence is indicated by the appearance of its properties.

For example: in the rusting of iron we meet with a typical chemical change since iron substance (gray, magnetic, and tenacious) goes out of existence as a different substance (reddish brown, crumbly, and nonmagnetic), commonly called iron rust, is made. Other commonly experienced changes which are chemical in nature are: the tarnishing of silver, the corroding of copper, and the burning of the carbon component of charcoal or coal.

Note.—Charcoal and coal are mixtures of carbon with nonburnable substances. Since the latter take no part in the burning phenomenon they are left behind in the mixture called ash.

Laboratory experiences as to changes that are chemical include: the burning of sulfur with iron, and the decomposition of water when an electric current is passed through it (p. 20). Let us gather convincing evidence that some of these phenomena do indeed involve chemical changes:

The tarnishing of silver. *Before the change,* the substance is silvery gray, shiny, and solid; *during the change,* a substance appears which is black, dull,

and solid. Conclusion: a different substance is made during the change, as evidenced by the appearance of a different set of properties, hence, *the change is chemical.* (This tarnishing can continue until there is no more silver.)

The burning of carbon. *Before the change,* the substance is black, solid, and burnable; *during the change,* a substance is made which is colorless, gaseous, and nonburnable. Conclusion: a different set of properties gives evidence of a *different substance* than that before the change, hence, *the change is chemical* in nature.

Decomposition of water (p. 20). *Before the change,* the substance is colorless, liquid, nonburnable; *during the change,* one substance is made which is colorless, gaseous, and burnable; and another substance which is colorless, gaseous, and will cause a wood splint, which is burning with glowing speed in air, to burn with a flame. Conclusion: the two resulting substances, with their different respective sets of properties, must be *different substances* from those before the change, hence, *the change is chemical* in nature.

These reasonings should serve as a pattern which can be followed for gathering evidence as to whether other matter changes are of the chemical change variety.

In the first two of the foregoing reactions all of the substances concerned were not taken into consideration nor was this necessary for the purpose intended. There is ample justification for concluding that the change is chemical if one can be made aware of the disappearance of only one substance, even though others may be going out of existence along with it, and of the appearance of only one of a possible two or several substances that are being made at the same time.

But let us now make note, by name, of all substances that participate in the three foregoing chemical changes, and assemble this information after the adopted word representation manner which is called the *word equation* for the reaction:

1. ***For the tarnishing of silver***

Silver + Hydrogen sulfide[1] → Silver tarnish + Hydrogen
(silver sulfide)

Interpreted: Silver reacts with hydrogen sulfide to make silver tarnish, or silver sulfide, and hydrogen.

2. ***For the burning of carbon***

Carbon + Oxygen → Carbon dioxide[1]

Interpreted: Carbon reacts with oxygen to make carbon dioxide.

3. ***For the decomposition of water***

Water → Hydrogen + Oxygen

Interpreted: Water decomposes to make the substances hydrogen and oxygen.

[1] In word equations, according to custom, in writing names of substances that contain two (or more) building materials, the first letter of the first-mentioned building material is capitalized, all others are small letters.

The word equation. Something more concerning the so-called word equation is in order at this time. To begin with, it is not really an equation in that no equality of materials before and after the reaction is indicated; that there is such an equality we shall see later (p. 19), but the word equation does not register this fact. Nor does this expression commonly represent conditions which make the reaction possible, such as whether the substances must be heated or exposed to light; nor, again, does it commonly tell of any accompanying phenomenon, such as whether heat, or light, or electricity is made along with the matter products, although such information may be introduced if desired (p. 97).

Thus, in the main, all that the word equation does accomplish is to mention in words and by name: (a) the substance or substances that exist before the reaction, and (b) the substance or substances that result therefrom. But, limited though this functioning may be, as a brief word record in respect to the reaction concerned, such an expression is a useful tool.

Incidental items to begin to think about. 1. *Substances and building materials.* Before going further it would be well to have some introduction (more of this on p. 31) to the custom of using the same name — such as iron, chromium, copper, silver, sulfur, carbon, oxygen — sometimes in respect to the substance, sometimes in respect to the building material[1] within the substance. For the beginning student this is a confusing practice, but the confusion will disappear in all due time. This custom arises from the fact that, when a substance is built of but one building material, the substance and the building material are usually given the same name. Accordingly, silver substance is built of silver building material, carbon substance is built of carbon building material.

2. *During a chemical change* a given substance or substances are destroyed as another substance or substances are made; but the building materials are not destroyed since during said reaction they simply find location in a different substance or substances. For example, in the following reactions:

Hydrogen sulfide +	Silver ⟶	Silver sulfide +	Hydrogen
↓	↓	↓	↓
the substance is destroyed. It is built of hydrogen and sulfur building materials which are not destroyed but find new locations, the sulfur in the hydrogen in	the substance is destroyed during the tarnishing. It is built of silver, the building material which is not destroyed but finds a new location in	the substance which is made.	the substance which is also made and which is built of hydrogen building material which is not made.

[1] Building materials are more commonly called elements (p. 38).

Carbon + Oxygen ⟶ Carbon dioxide

Carbon	Oxygen	Carbon dioxide
the black substance is destroyed during the burning. It is built of carbon building material which is not destroyed but enters into	the substance is destroyed; not so, oxygen, the building material, which also enters into	the substance, which is made.

3. *The ending ide* has come to be applied to the names of substances that contain only *two building materials* in their make-up. Thus, silver sulf*ide* means that this substance is built of the two building materials silver and sulfur; sodium chlor*ide* means that this substance is built of the two building materials sodium and chlorine. There is an exception to this rule which will receive mention later. *The ending ate* usually signifies the presence of *oxygen as a third building material* within the substance (p. 37).

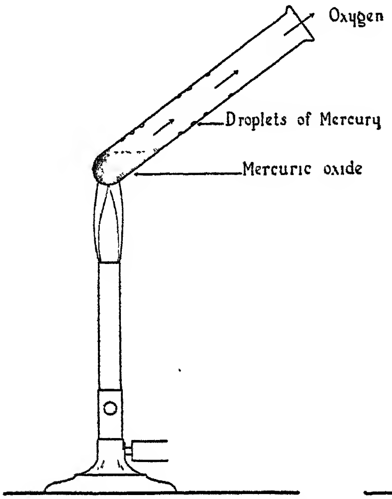
Types of chemical change. For various reasons it is helpful in the study of chemistry to be able to classify chemical changes from the standpoint of selected similarities. For example: the reactions which take place in the rusting of iron with oxygen, the burning of carbon with oxygen, and the burning of sulfur with iron are of the same type in that during the reaction, in each case, two substances go out of existence whereas only one substance is made; or, in the language of the chemist, *two substances combine to make one substance.* The label that has been given to *this type of reaction is that of direct combination,* and many reactions are of this type. Word equations for above reactions are as follows:

Iron + Oxygen → Iron oxide
Carbon + Oxygen → Carbon dioxide
Sulfur + Iron → Iron sulfide

But there are also many reactions, after the manner of the decomposition of water (Fig. 8), in which only one substance exists before the reaction while two substances and sometimes more than two substances are made. Another reaction of this type is involved when mercuric oxide is heated until it *decomposes* to make the substances mercury and oxygen (Fig. 1). Still another reaction of this type occurs when cane sugar is heated in a test tube or, more familiarly, when candy boils over on the hot stove or the pie boils over in the oven. During such heating, the cane sugar, if it is kept at a sufficiently high temperature, *decomposes* to make a number of substances, some of which are mentioned in the pictured representation of this phenomenon in Figure 2, also in the partial word equation for the reaction which accompanies

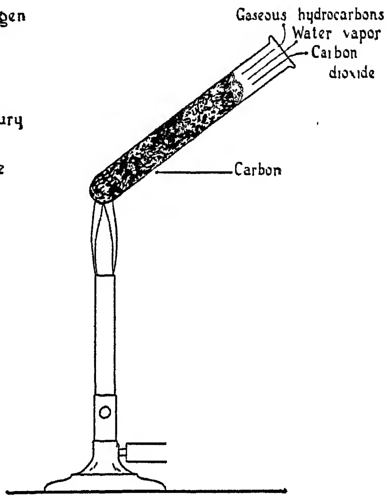
the same. *Reactions of this type, in which one substance goes out of existence as two or more substances are made, are called decomposition reactions.*

A caution: Decomposition is a label that is frequently used carelessly in respect to reactions that are not of the type described. For example: the spoilage of meat does not involve a decomposition reaction (p. 80).



Mercuric oxide → Mercury + Oxygen

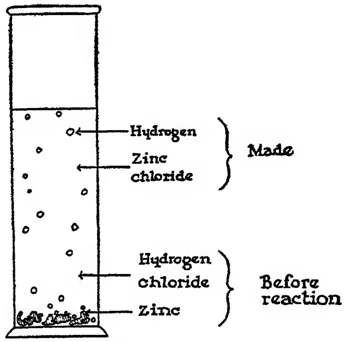
FIG. 1. Decomposition of Mercuric Oxide



Cane sugar → Carbon + Hydrocarbons
+ Water + Carbon dioxide
+ Many other substances

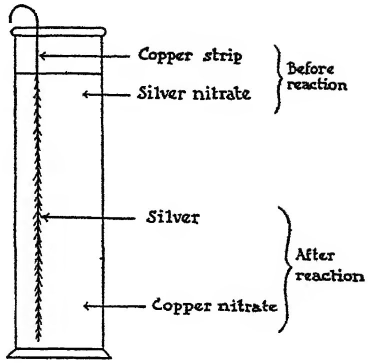
FIG. 2. Decomposition of Cane Sugar

Another type of reaction is exemplified by the tarnishing of silver. During this reaction silver building material from silver substance displaces hydrogen from hydrogen sulfide to make black silver sulfide; at the same time the hydrogen thus displaced builds itself into the gaseous substance hydrogen (p. 14). Two other reactions of this type occur when zinc is in contact with hydrogen chloride, and when copper is in contact with silver nitrate (Figs. 3 and 4); in the former, zinc building material from zinc substance displaces hydrogen building material from hydrogen chloride, as the result of which hydrogen, the substance, and zinc chloride are made. During the latter reaction, copper building material from copper substance displaces silver from silver nitrate, as the result of which silver, the substance, and copper nitrate are made. *Such reactions are called displacement reactions.*



Zinc + Hydrogen chloride → Hydrogen + Zinc chloride

FIG. 3. Reaction of Zinc with Hydrochloric Acid



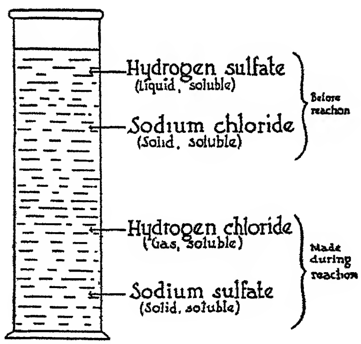
Copper + Silver nitrate → Silver + Copper nitrate

FIG. 4. Reaction of Copper with Silver Nitrate

The fourth type of chemical reaction takes place between two substances each of which is composed of two parts in more or less loose combination. When substances of this variety such as

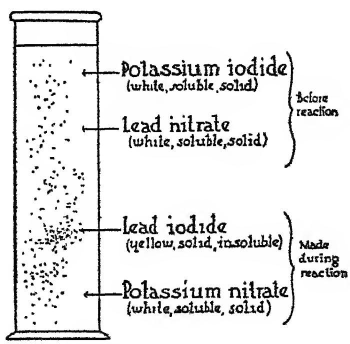
$$\overbrace{\text{Hydrogen} \cdot \text{sulfate}}^{(1)\qquad\quad(2)} \quad \text{and} \quad \overbrace{\text{Sodium} \cdot \text{chloride}}^{(1)\qquad\quad(2)}$$

are in contact with each other in water solution a "change of partner" reaction takes place in which *the two parts of the two substances change places,* thereby making two other substances. These reactions between hydrogen sulfate and sodium chloride, and between potassium iodide and lead nitrate are described in Figures 5 and 6 in detail.



Sodium chloride + Hydrogen sulfate → Sodium sulfate + Hydrogen chloride

FIG. 5. Reaction of Sodium Chloride with Sulfuric Acid



Potassium iodide + Lead nitrate → Lead iodide + Potassium nitrate

FIG. 6. Reaction of Potassium Iodide with Lead Nitrate

Hundreds of reactions of this type occur and the label generally applied to them is that of *double decomposition.* This is an unfortunate label, in a way, in that reactions of this type have no relationship to the decomposition reactions of previous discussion.

There are other types of reactions; also, there are many reactions which are individualistic in that they follow no specific type. But these four types presented will suffice for our purposes and they will be represented generously in the reactions of our future study.

FUNDAMENTAL FACTS IN REGARD TO CHEMICAL CHANGE

Ever since the beginnings of chemistry science, chemists have been studying reactions from various aspects in a continual search for factual information concerning the same; and their findings to date, obtained many times as the result of a tremendous amount of very careful laboratory investigation, constitute a large part of our science heritage.

Thus, one important question that has been answered has to do with why it is that, during chemical changes, substances before the reactions must go out of existence as the new substances are made. And the answer obtained is that the beginning substances hold within their keeping the needed building materials which, during the reactions, are taken from said substances to be built into the resulting substances (p. 14). Two examples of this fact are provided in the detailed study of the tarnishing of silver (p. 14) and the burning of carbon (p. 15). Another example is provided in the rusting of iron, during which reaction nature takes the iron and oxygen building materials from iron and oxygen substances, respectively, and builds them into the one substance, iron oxide:

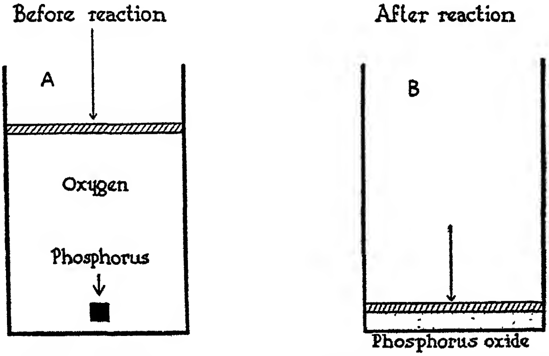
$$\underbrace{\text{Iron}}_{\substack{\downarrow \\ \text{contains iron} \\ \text{building material}}} \text{ (substance)} + \underbrace{\text{Oxygen}}_{\substack{\downarrow \\ \text{contains oxygen} \\ \text{building material}}} \text{ (substance)} \rightarrow \underbrace{\text{Iron oxide}}_{\substack{\downarrow \\ \text{contains iron and oxygen} \\ \text{building materials}}} \text{ (or Iron rust)}$$

Therefore, while it is true that during chemical reactions some substances are destroyed and other substances are made, the same is not true of building materials (pp. 21 to 22).

Law of conservation of mass. Another question in which chemists have interested themselves, and for which they have taken great pains to find an answer, has to do with the relationship between the quantities of substances that go out of existence and the quantities of substances that are made in the course of a chem-

ical reaction. This investigation necessitates weighing substances very carefully before the reaction and weighing the resulting substances and, obviously, great care must be taken not to lose one iota of the beginning or resulting substances. The following are limited presentations of two examples of the results of such measured findings:

1. When phosphorus reacts with oxygen, the product is phosphorus pentoxide, a white, solid substance. This reaction takes place slowly at ordinary temperatures. Now suppose that weighed amounts of phosphorus and oxygen — in the exact proportions in which they react — are put into a closed container, and suppose their inclusive weight is 4 grams (Fig. 7A). Then let these



The inclusive weight of these two substances is 4 grams.

The phosphorus oxide product weighs 4 grams.

Fig. 7. Reaction of Oxygen with Phosphorus

two substances remain in contact with each other until combination is complete, when there will be no phosphorus present or oxygen but only phosphorus pentoxide. Finally, when this substance is weighed it will be found to weigh exactly 4 grams (Fig. 7B). (If either phosphorus or oxygen were in excess of the exact proportions for reaction, the final weight, in this instance 4 grams, would be the inclusive weight of phosphorus pentoxide product and the excess phosphorus or oxygen.)

2. Again, let us consider measured findings in respect to the decomposition of water to make hydrogen and oxygen, the substances (Fig. 8). If 12 ounces is the weight of the water to begin with, and if its decomposition is continued until no water is left, the inclusive weight of hydrogen and oxygen then obtained will be found to be exactly 12 ounces. Thus, the inclusive weight of the two substances, hydrogen and oxygen, that result from this reaction is identical with the weight quantity of the beginning water.

These quantitative findings are in accordance with all such as have been made in respect to chemical reactions: namely, *the inclusive weight of* **substances** *mutually involved before a reaction is exactly equal to the inclusive weight of the* **substances** *that result from*

said reaction. This constitutes another of the factual discoveries that are fundamental to chemistry science, and the label that has come to be applied to this fact is the *Law of Conservation of Mass.*

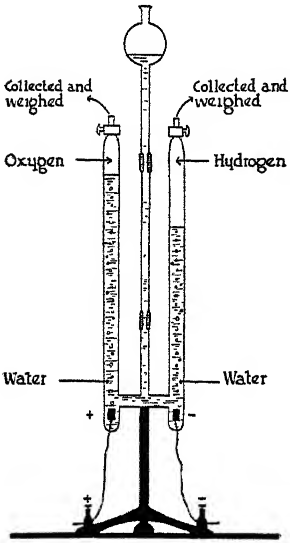


FIG. 8. Decomposition of Water by Electrolysis

The making of such studies as these is not as simple as the foregoing presentation may suggest. They require as accurate weighing means as man can devise, skilled workmanship is essential, and no leakage on the part of any substances concerned can be tolerated. Indeed, every chemical reaction that has been subjected to such measurings, with correct results obtained, is a distinctly creditable experimental achievement.

Law of chemical change. The explanation for this equality in weight of substances before and after a reaction points directly to the building materials therein, and to the fact that ***building materials,*** *commonly called* ***elements,*** *neither lose nor gain in weight, as they pass from the beginning substance or substances to another substance or substances, during the course of a chemical change* (p. 14). This constitutes another fundamental fact of chemistry, which is called the *Law of Chemical Change.* It is applied to the two reactions studied, as follows:

1. In the reaction of phosphorus with oxygen to make phosphorus pentoxide:

In substances before reaction		*In substances after reaction*
Phosphorus substance +	Oxygen substance →	Phosphorus pentoxide substance
(these two substances weigh inclusively 4 grams because		(this substance weighs 4 grams because ↓ it is built of the entire supply of *phosphorus and oxygen elements* previously within the two beginning substances
contains phosphorus building material or *element*	*contains oxygen* building material or *element*	
the inclusive weight of the two elements within these substances is 4 grams.		a total of 4 grams of these two elements.

2. In the decomposition of water to make hydrogen and oxygen:

In substances before reaction	*In substances after reaction*	
Water the substance →	Hydrogen the substance +	Oxygen the substance
(weighs 12 ounces because) ↓	(these two substances weigh inclusively 12 ounces because) ↓	↓
it is built of *hydrogen and oxygen elements*	contains all of the *hydrogen element* previously in water	contains all of the *oxygen element* previously in water
the inclusive weight of which is 12 ounces.	the inclusive weight of the two elements within them is still 12 ounces.	

Thus does the fact of conservation of mass meet with an explanation in the fact of chemical change. But these two fundamental facts must not be confused, nor is there any necessity for confusion; the former fact refers to ***substances**, which are respectively destroyed and made;* the latter fact looks within said substances, to their ***building materials or elements**, which are not destroyed*, but are taken from the beginning substance or substances for the making of the resulting substance or substances.

That these two facts have always been consistently observed by nature, in the course of chemical reactions, is undoubtedly true; but man's discovery of these facts is of comparatively recent date. And certain it is that these discoveries, and man's consequent understanding insight into the ways of nature in respect to chemical reactions, from the viewpoint of quantitative involvements of substances and elements concerned, have contributed greatly to the progress of scientific study, and to the progress of the industrial concerns of the world during the past one hundred and fifty years. Nutritionists and animal and plant physiologists now know that, in respect to every reaction that takes place in the cells of animals and plants, the inclusive weight of substances entering a reaction must be equal to the inclusive weight of substances emerging from said reaction. They know, too, that any given quantity of an element — iron, or oxygen, or iodine, or nitrogen — must remain consistently that same quantity of said element as it passes from one substance into another substance or substances in the sequence of reactions that occur here and there within plants and animals. In industrial interests, this awakening to the quantitative involvements of substances and building materials, in respect to reactions, has played its own

fundamental part in placing modern manufacturing on a known calculated basis with no uncertainty as to the quantitative outcome in the way of products. How different this is from the manufacturings of prechemistry days, before these quantitative considerations were known, when manufacturers were obliged to depend solely upon handed-down recipes, the development of years or even centuries of trial and error procedures, which many times would, and many times would not, result in anticipated products as to kind and quantity.

Speed of chemical reactions. There are various factors that determine the speed with which a chemical reaction takes place; certain of these we shall consider at this time.

A most important speed factor lies in the *tendency of the substance or substances to engage in reaction:* the greater their tendency to react the greater the speed of reaction and vice versa. For example:

1. When the same quantities of cane sugar and mercuric oxide (p. 16) of the same degree of fineness are put into separate test tubes and heated to exactly the same temperature, the cane sugar will decompose more rapidly than the mercuric oxide due to the fact that, of these two compounds, cane sugar has the greater tendency to decompose.

2. Again, both magnesium and zinc react with hydrochloric acid to make hydrogen as one product. But — provided the magnesium and zinc present the same surface areas to the acid and the acid is of the same concentration — reaction between magnesium and hydrochloric acid takes place more rapidly than between zinc and said acid (Fig. 56, p. 189). And the reason is that magnesium and hydrochloric acid have a greater tendency to engage in reaction than have zinc and this acid.

A second speed factor, and the one that is most familiar, has to do with *the temperature of the substance;* in other words, the higher the temperature of the substance or substances concerned the greater is the speed of reaction and vice versa. Thus:

1. Neither cane sugar nor mercuric oxide decomposes with appreciable speed at ordinary temperatures; but when their temperature is raised sufficiently reaction does begin to be appreciable, with the speed of their decomposition increasing continuously as these substances get hotter and hotter.

2. All reactions, as to proteins of meat and similar foods, that are responsible for food spoilage take place more rapidly on warm days than on cold ones; and less rapidly in the refrigerator than on the pantry shelf.

3. Of vital significance is the fact that metabolic reactions take place more rapidly in the cells when the body is suffering under the higher temperatures that prevail in fever than when it is at normal temperatures. Evidence of this fact is the continual decrease in weight of the body thus afflicted.

A third speed factor is concerned with the *area of the substance that is presented to the reaction:* the greater the area of the one

substance affected or the greater the area of contact between substances, should two or more be involved, the greater the speed of reaction and contrariwise. So it is that the breaking up of large lumps of substances, grindings or stirrings of the same, and getting substances into solution provided they are soluble, are all means that are employed for increasing reaction speeds. For example:

1. The speed of decomposition of mercuric oxide (Fig. 1) is determined not only by the temperature of this substance but also by its degree of fineness: the smaller the particles of mercuric oxide and the greater the number of particles of this substance that are heated, the greater is the speed of reaction.

2. Again, the total reaction between potassium iodide and lead nitrate (p. 17) to make the resulting matter products takes place almost instantaneously due to the fact that both substances are spread out in solution, hence are in maximum contact with each other.

Finally, there are instances of reactions that are speeded-up or speeded-down by the presence of specifically selected substances called *catalytic agents*. But the study of this phenomenon will be left until later (Chapter V).

Questions

1. What distinguishes a chemical change from a physical change?
2. Which of the following changes are physical and which are chemical in nature? Give convincing reasoning in each instance:
   a. The corroding of copper.
   b. The disappearance of moth balls shut up with stored clothing.
   c. Burning of the celluloses of wood
   d. Preparation of French dressing.
   e. Burning of a candle.
   f. Heating of an iron.
3. What information regarding a chemical reaction is provided by the word equation? Interpret the following:
   a. Mercury + Iodine → Mercury iodide.
   b. $\begin{matrix}\text{Hydrogen}\\\text{sulfate}\end{matrix} + \begin{matrix}\text{Sodium}\\\text{chloride}\end{matrix} \rightarrow \begin{matrix}\text{Sodium}\\\text{sulfate}\end{matrix} + \begin{matrix}\text{Hydrogen}\\\text{chloride}\end{matrix}$
4. Interpret the word equations given on page 26.
5. Assemble word equations for all reactions studied in this chapter for which sufficient information is provided and classify these reactions, when possible, as to the four types of chemical change studied.
6. What building materials are contained in the substance water? What becomes of these building materials when water decomposes?
7. State the law of conservation of mass and illustrate with reference to:
   a. The decomposition of mercuric oxide.
   b. The burning of carbon.
   c. The tarnishing of silver.
8. State the law of chemical change and illustrate with reference to:
   a. The burning of sulfur.
   b. The reaction of zinc with hydrogen chloride.

9. In respect to each of the following, tell which will weigh more, and give the reason:

a. A silver spoon before or after tarnishing.

b. A gram of mercuric oxide or the mercury resulting from its decomposition.

c. The potassium iodide and lead nitrate before a reaction or the resulting potassium nitrate and lead iodide.

10. Name four factors that affect the speed of a chemical reaction, telling how each functions. Give specific examples.

11. How does refrigeration function in respect to food spoilage? Give examples.

CHAPTER III

Simple Substances. Compounds. Elements

Having had some introduction to *substances,* what they are and how to recognize them, and to *chemical changes* with important items concerning the same, let us return to the further study of substances; then let us follow this study with some information in regard to *building materials* for substances.

Kinds of substances. The number of substances that are possible may be endless: hundreds exist already made in earth's crust; eight are always present in earth's atmosphere, usually more; earth's waters hold in solution and in suspension dozens of substances, most of which have been washed out from earth's solid crust; plants and animals are aggregates of many substances; finally, from materials provided by nature, man has made thousands of substances many of which had never been in existence until their birth in a laboratory. But even though these thousands of substances are possible, they all, from one classification viewpoint, fall into *two* groups: namely, *simple substances* and *compound substances* or compounds.

SIMPLE SUBSTANCES

Among simple substances of common occurrence are the following:

Copper — reddish brown, solid, subject to tarnishing
Iron — gray, magnetic, solid, subject to rusting
Aluminium — gray, nonmagnetic, solid
Carbon — black, solid, burns with oxygen

And these are classed as simple substances because up to the present time no one has been able to make the substance copper, or the substances iron and aluminium, or the substance carbon by the direct combination of two or more other substances; nor has any one been able to decompose any one of these substances into two or more other substances. Of course, as all informed people know, the substances copper and iron can be made, and have been made for hundreds of years; so, also, can aluminium be made, and

has been for about a hundred years; and carbon is made every time wood or sugar chars; but not one of these substances has ever been made by the means defined.

The following word equations, which represent reactions whereby these substances can be made, indicate that the reactions are not of the direct combination type:

Copper oxide + Hydrogen → Copper + Water
Iron oxide + Carbon → Iron + Carbon dioxide
Aluminium oxide + Silicon → Aluminium + Silicon dioxide
Sugar → Carbon + Many other substances

A *simple substance*, then, is a substance which *can neither be made by the direct combination of, nor be decomposed into, two or more other substances.* By way of further examples: *oxygen,* the gaseous substance which comprises one-fifth of the atmosphere, is classed as a simple substance because no one has ever made it by the direct combination of other substances nor has any one been able to decompose it into two or more other substances. *Mercury,* silvery, and a liquid; *chlorine,* greenish yellow, gaseous, and with a characteristic odor; *sulfur,* yellow, odorless, and solid — are, also, simple substances because of like findings.

How many simple substances are there? The number of simple substances is decidedly limited. The reason for this is difficult to explain but suffice it to say that, generally, although not always, nature seems to prefer to build but one simple substance from any one given building material or element. Accordingly, there is one iron substance built of the one iron building material, one copper substance built of the one copper building material. If, therefore, this situation held right straight through, only as many simple substances would be possible as there are building materials, or ninety-two. But there are exceptions, in that there are some instances of two or more simple substances which are built of the same element. For example:

Oxygen — gaseous and odorless *Ozone* — gaseous, with a fresh odor	are two simple substances made of the same building material, namely oxygen.
Carbon — black, dull, solid *Graphite* — black, lustrous, solid *Diamond* — colorless, crystalline, hard	are three simple substances made of the same building material, namely carbon.
Yellow phosphorus — solid, active chemically *Red phosphorus* — solid, inactive chemically	are two simple substances made of the same building material, namely phosphorus.

Thus the total number of simple substances counts up to somewhat over a hundred. But even so, a hundred and more simple substances are relatively few in comparison with the thousands, and more thousands, of substances of the compound variety.

How many are commonly known? That is, how many simple substances thrust themselves so conspicuously and so persistently into the everyday living affairs of most people as to render personal and conscious acquaintance with them almost unavoidable? Certainly such a list of *simple substances* would include most of the following:

Aluminium	Iron	Oxygen (?)
Carbon	Lead	Platinum
Chromium	Mercury	Silver
Copper	Nickel	Tin
Gold	Nitrogen (?)	Zinc

Nitrogen and oxygen are questioned, because, being the colorless, odorless, tasteless, and gaseous substances that they are, they do not thrust themselves unavoidably upon the attention. But, when mentioned, many people would be able to say: "Of course, oxygen is the substance in the air that functions with so many other substances in burning"; they might also be able to say: "Certainly, nitrogen is another of the atmosphere's gaseous substances"; but quite likely they would be less ready with a convincing description of either of these substances. However, we will credit many people with as conscious an acquaintance with these simple substances as is possible in view of their native inconspicuousness.

But even including oxygen and nitrogen, the foregoing fifteen simple substances are about the only ones that are commonly recognized. Among the remaining substances of this variety, *iodine*, a purplish black solid, and *manganese*, a grayish white solid, really do contribute to materials of common usage; but most people have not become consciously acquainted with them as individual substances, due to the fact that they are obscured by mixed association with other substances. This is true of iodine in tincture of iodine, which is a solution of iodine in alcohol, and of manganese, which is commonly alloyed with iron in stainless steel.

Most simple substances — including hydogen, which is gaseous and burns with oxygen, and sulfur which is yellow, solid, and burns with both oxygen and iron — are met with only by workers in laboratories or in industries in which they are used; consequently,

acquaintance with them is the exceptional rather than the usual experience.

Physical state. About ten simple substances — oxygen, nitrogen, hydrogen, chlorine, and helium among them — are *gaseous* at ordinary temperatures, but can be obtained in liquid and solid states at sufficiently low temperatures. (See accompanying table.) Two simple substances are *liquid:* the well-known silvery liquid mercury; and the less well-known bromine, which is reddish brown, liquid, very volatile, and dangerously caustic. All other simple substances are *solid* at ordinary temperatures: some of these solid substances, such as phosphorus and sulfur, can be obtained in the liquid and gaseous states at easily obtained elevated temperatures; but others, such as aluminium, copper, nickel, and iron, remain solid up to very high temperatures. Herein lies one reason for the use of these latter metal substances for the making of utensils and containers that are to meet commonly with high temperatures.

	Solid below	*Liquid below*	*Gaseous*
Oxygen	– 219° C.	– 183° C.	
Nitrogen	– 210° C.	– 196° C.	at ordinary
Hydrogen	– 260° C.	– 253° C.	temperatures
Helium	– 273° C.	– 269° C.	
	Solid below	*Liquid*	*Gaseous above*
Bromine	– 8° C.	at ordinary	59° C.
Mercury	– 39° C.	temperatures	357° C.
	Solid	*Liquid above*	*Gaseous above*
Sulfur		113° C.	445° C.
Aluminium	at ordinary	660° C.	1800° C.
Copper	temperatures	1083° C.	2300° C.
Iron		1535° C.	3000° C.

Classification. The differentiating labels *metals* versus *nonmetals*, when used in reference to substances (p. 2), apply only to simple substances.

In the original and ancient use of the label *metals* in respect to the few such substances as were known long ago, chiefly iron, copper, silver, lead, and tin; also in the general use of this label today in respect to a longer list of substances, there was and is a purely *physical significance.* Thus, metals have come to include substances which are capable of a high polish, which are good conductors of heat and electricity, and which, when solid, are malleable and ductile; nonmetal substances, therefore, have come to mean such as do not meet these property specifications.

But, despite this purely physical implication in the line-up of substances as metals or nonmetals, it has been discovered that the substances classed as *metals do react in chemical ways in characteristically similar and dissimilar manners,* quite unlike the chemical behaviors of substances classed as nonmetals. As a result, this classification of simple substances has come likewise to have a *chemical significance* which, while not entirely satisfactory, has its helpful aspects in chemistry study, as will be found to some extent presently, and more convincingly later.

These are metal substances:

Potassium — bluish gray, shiny, soft, solid
Sodium — gray, shiny, soft, solid
Barium — yellowish, shiny, solid
Calcium — silvery gray, hard, solid
Magnesium — shiny, gray, solid
Aluminium
Zinc
Chromium (See question 4, page 48.)
Iron
Nickel
Tin
Lead
Arsenic — dark gray, solid
Copper
Mercury
Silver
Platinum
Gold

These are nonmetal substances:

Sulfur — yellow, solid
Phosphorus — yellowish white, solid
Carbon — black, lusterless, solid
Chlorine — greenish yellow, gas
Bromine — reddish brown, volatile, liquid
Iodine — purplish black, volatile, solid
Nitrogen — colorless, gas
Helium — colorless, gas

Chemical activity. The expressions *very active, active,* and *inactive,* as to the chemical behavior of substances, have doubtless come to stay as part of the language of chemistry. But they are subject to a difference in usage, hence it is not surprising that for beginning students they are vague and misunderstood; even so, these expressions are useful and are encountered frequently in chemistry literature. It is essential, therefore, to begin to make them as meaningful as possible as we use and apply such expressions, first in respect to the chemical behavior of simple substances, and later in respect to compounds.

Among metal substances. The above metal substances are listed according to their comparative chemical activities. *Potassium, sodium, and calcium are very active* chemically since they react very readily, even at ordinary temperatures, with quite a number of substances — oxygen, water, and acids among them. Of these three substances, potassium is the most active, with sodium a close second, and then calcium. Incidentally, because of their great chemical activity, these substances can never meet with any practical uses in everyday concerns; while in laboratories

they must be used with great caution, and supplies not in use must be stored with great care. *Aluminium, zinc, and iron are less active* than the above mentioned metal substances. This is evidenced by the fact that, when these metals are placed in contact with the same selection of substances as are provided for potassium, sodium, and calcium, reactions are less rapid; at ordinary temperatures aluminium, zinc, and iron react very, very slowly with water and with oxygen; with some acids reactions proceed slowly, with others rapidly. Of these metal substances aluminium is the most active, zinc next, and then iron. *Silver, platinum, and gold are inactive* chemically because they react appreciably with few substances and with most of these very slowly; with oxygen they do not react at all nor with water, even at the highest temperatures obtainable. If, therefore, platinum could be obtained as plentifully as are aluminium and iron, what admirable cooking utensils and other metal containers it would make, and how splendid it would be for metal fittings and metal structures of all sorts!

Silver and gold, even if plentiful, would not be as practical for various uses as platinum. Gold, while inactive chemically, is very soft. Silver is likewise soft; also, while generally inactive, it does react readily with one commonly occurring substance, namely hydrogen sulfide, to make the black tarnish, or silver sulfide, which is so familiar (p. 13).

Chemical activity of nonmetal substances. *Yellow phosphorus is chemically very active* because it reacts readily with quite a number of substances, including oxygen. *Sulfur, oxygen, and hydrogen are inactive* at ordinary temperatures but *active* at elevated temperatures, since they react with other selected substances either slowly or inappreciably at ordinary temperatures but rapidly at elevated temperatures. *Chlorine, bromine, and iodine are inert in respect to oxygen,* meaning that they do not react with it at all; but they are from *more to less active in respect to metal substances.* Chlorine reacts with all metal substances, vigorously with those high in the scale of activity, more slowly but still appreciably with those metals which are less active; for this reason, the persistent presence of excess chlorine in water for disinfection purposes will in time result in appreciable reaction with metal fittings in the plumbing; also, when chlorine is used for bleaching, it may react appreciably with surface layers of any silver, gold, or platinum jewelry that may be at hand. Bromine is less active than chlorine, and iodine even less so, in reaction with the same metals. All three

of these substances are *very active in respect to proteins;* hence the effectiveness of chlorine and iodine as disinfectants since they react readily with the proteins of bacterial cells; hence, too, the severe burns that follow when bromine is spilled on skin areas and when iodine is used too lavishly, since bromine and iodine attack the proteins of skin. Bromine is also an effective disinfectant, but it is more hazardous to handle than either chlorine or iodine.

Fluorine, chlorine, bromine, and *iodine,* called the "halogens," comprise a *chemical family* of substances because of their similar "likes" and "dislikes" in respect to reacting partner substances. Their chemical activities vary from fluorine, which is dangerously active, to iodine, which is the least active of these halogen substances.

Finally, there are a few simple substances which are the *extreme of chemical inactivity.* Among these are *helium, argon,* and *krypton,* which are colorless, gaseous substances and which comprise a very small portion of the earth's atmosphere; all three are *inert* chemically in that they do not engage in any reactions with other substances.

A summary as to chemical activities. 1. A chemically *active substance* means one which reacts fairly speedily with quite a selection of other substances, not by any means with all substances.

2. An *inactive substance* means one which reacts appreciably with a very limited number of substances.

3. *Temperature* is an *important factor* in that a given substance may be inactive at ordinary temperatures but active at higher temperature levels.

4. A *few substances are chemically inert* in that they react either with great difficulty or not at all with other substances.

Composition of simple substances. *A simple substance is composed of just one variety of building material* which commonly, but not always, has the same name as the simple substance. Accordingly, carbon substance is built of the one building material, likewise called carbon; copper substance is built of the one building material called copper. These are review items of previous presentation (p. 26).

Synonymous expressions. And now the time has come to say that the label which we have been using for this variety of substance, namely *simple substance,* is not the one in common use, which is *element.* But, unfortunately, *this word element is used with two meanings:* sometimes in reference to the simple substance, which as a substance has a distinctive set of properties and can therefore

make itself evident; sometimes in reference to the building material within a substance of which one cannot become aware. Thus, in general practice, iron element may on occasion be used in reference to iron simple substance, which, because it is silvery gray, magnetic, and capable of rusting, is able to make itself evident; while, at other times, the user of the expression iron element may have in mind the iron building material which has no properties but is present within substances: within iron oxide, or iron chloride, or within other iron-containing substances.

This is all very confusing for the beginning student of chemistry since element, the substance, is by no means element, the building material, a fact that will become more convincing as this study progresses. Some people attempt to avoid this confusion by using *free element* for the simple substance, and just *element* or *combined element* for the building material. Naturally, students should be aware of these practices if they are to read, with understanding, books dealing with chemistry. Fortunately, most adopted words and expressions, that are peculiar to the chemistry language, carry the same meaning for all informed users of the chemistry vocabulary; but occasionally there is a confusion of usage: the use of the word element is one of these instances. In order to avoid this confusion, *this text will use the expression simple substance only when the substance is intended and the word element only in respect to the building material.*

COMPOUND SUBSTANCES OR COMPOUNDS

Defined. In contrast with the defined specifications for a simple substance (p. 26), *a compound substance is a substance which can either be made by the direct combination of two or more substances or can be decomposed into two or more substances* by ordinary chemical means, that is, by the use of such agents as heat, electricity, or light. For example: according to these specifications, and consulting reactions previously studied, *carbon dioxide* is a compound substance since it can be made by the direct combination of the two substances carbon and oxygen (p. 15); *iron sulfide* is a compound because it can be made by the direct combination of the two substances sulfur and iron (p. 15); *copper sulfate hydrate* is a compound because it decomposes to make the two substances copper sulfate and water (p. 178); *cane sugar* is a compound because, when heated sufficiently (oxygen excluded), it decomposes to make carbon, water, and many other substances (p. 16).

Composition of compounds. In contrast with a simple substance, *a compound is built of two or more elements (building materials)*. A given compound is nonetheless a single substance with a single set of properties that are characteristic of it, the elements within the compound having no separate individuality. *Cane sugar*, for example, is composed of the three elements carbon, hydrogen, and oxygen but these elements exhibit no properties as is well known, since one cannot see or become aware of their presence in any way; it is the cane sugar which makes itself known as a single entity with one set of properties; the carbon, hydrogen, and oxygen are, therefore, but the constituent elements while the cane sugar is the substance. And again, *sodium chloride* is composed of the two elements sodium and chlorine, which in no way indicate their presence; it is the sodium chloride which has the personality features — white, solid, salty taste, and soluble; hence it is the sodium chloride which is the substance, the sodium and chlorine being its constituent building materials.

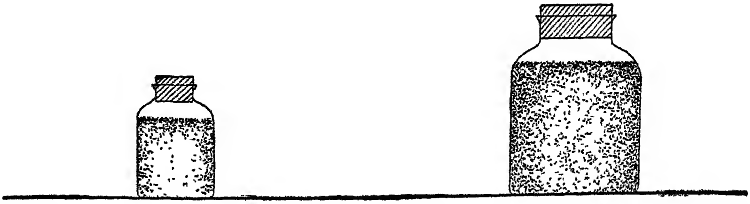
Many compounds contain but two elements; many more are built of three elements, in which case oxygen is usually one of them; fewer compounds are composed of four elements; and occasionally there are compounds built of more than four elements. But in the main nature draws upon only two or three elements for the making of a compound. For example:

The compound	*contains the two elements*
Water or Hydrogen oxide	hydrogen and oxygen
Iron oxide or iron rust	iron and oxygen
Silver sulfide or silver tarnish	silver and sulfur
Calcium carbide	calcium and carbon
Sodium chloride	sodium and chlorine

The compound	*contains the three elements*
Potassium chlorate	potassium, chlorine, and oxygen
Potassium chlorite	potassium, chlorine, and oxygen
Copper sulfate	copper, sulfur, and oxygen
Silver nitrate	silver, nitrogen, and oxygen
Any carbohydrate	carbon, hydrogen, and oxygen

Quantitative composition. In regard to the quantitative make-up of compounds, nature builds in a very fixed and definite manner. Not only is a given compound composed of a definite selection of elements but in all specimens of the compound the given elements are always present in the same definite weight proportions. Thus:

Within all specimens of *sodium chloride* the constituent elements sodium and chlorine are present in weight proportions of 39.34 to 60.66 (Fig. 9).



Within 1 ounce of sodium chloride	Within 10 ounces of sodium chloride
weight of sodium : weight of chlorine	weight of sodium : weight of chlorine
as	as
39.34 : 60.66	39.34 : 60.66

FIG. 9

Within *cane sugar* the constituent elements hydrogen, carbon, and oxygen are present in a weight proportion of 42.10 to 6.48 to 51.42; therefore, within any mass whatsoever of cane sugar — whether one ounce or six ounces, one gram or fifty grams, eight tons or twenty-five tons — 42.10 per cent of the total weight is the element carbon, 6.48 per cent is the element hydrogen, and 51.42 per cent is the element oxygen (Fig. 10).

Within 1 gram of cane sugar	Within 12 grams of cane sugar
weight of carbon : weight of hydrogen : weight of oxygen	weight of carbon : weight of hydrogen : weight of oxygen
as	as
42.10 : 6.48 : 51.42	42.10 : 6.48 : 51.42

FIG. 10

And the same condition holds for every compound in existence, in that: *within every specific compound the elements concerned are present in the weight proportion in respect to each other, hence in respect to the compound as a whole, that is definite and fixed for said compound.* This fact has come to be called the *Law of Definite Weight Proportions.*

It follows from the foregoing that if ever the same selection of elements should be found in combination in two, or three, or several differing weight proportions then two, or three, or several different compounds are involved. *Carbon dioxide* and *carbon monoxide,* for example, are composed of the same elements, yet they are totally different substances as everyone very well knows;

carbon dioxide is harmless physiologically, indeed it is a product of plant and animal living, it will not burn; carbon monoxide is poisonous in that with sufficient intake the animal dies, it will burn. And that which is chiefly responsible for their being two different substances lies in the differing weight proportions between the carbon and oxygen constituent elements within these two compounds. So, also, are *water* and *hydrogen peroxide* two different substances, but made of the same constituent elements: water is odorless and tasteless as to physical properties and chemically stable (p. 36); hydrogen peroxide has an odor and taste and is unstable. And the reason that these two compounds are different substances lies largely in the fact that the weight proportion between the hydrogen and the oxygen in water is 11.19 to 88.81 whereas in hydrogen peroxide it is 5.93 to 94.07. Again, *calomel* contains the same constituent elements as does *corrosive sublimate*, both are *mercury chlorides* but they are two different substances; physically, both are white solids, but they have different solubilities and densities; chemically they react differently; physiologically, calomel can be used medicinally, while corrosive sublimate will kill. And once again, one reason why these are different substances lies in the fact that they are built of different weight proportions of their commonly contained constituent elements, mercury and chlorine:

Carbon dioxide		*Carbon monoxide*	
27.29 to	72.71	42.88 to	57.12
parts by weight of carbon	parts by weight of oxygen	parts by weight of carbon	parts by weight of oxygen
Hydrogen oxide (Water)		*Hydrogen peroxide*	
11.19 to 88.81		5.93 to 94.07	
Mercurous chloride		*Mercuric chloride*	
84.98 to 15.02		73.9 to 26.1	
Carbo hydr ate (Cane sugar)		*Carbo hydr ate* (Glucose)	
42.10 to 6.48 to 51.42		40 to 6.71 to 53.29	

Chemical behavior. The chemical behavior of compounds can be considered under two headings: their *chemical activity* and their *chemical stability*. These terms are frequently confused, therefore, it is advisable to give them definite and differentiated meanings, and then to use them consistently with these meanings.

Chemical activity of compounds, as well as of simple substances (p. 29), has reference to the tendency of the substances to react

with other substances. If a compound substance reacts with quite a good many other substances fairly speedily it can reasonably be called chemically *active;* if it reacts with only a few substances and then usually quite slowly, it is *inactive.* And as with all substances, *temperature* is an activity factor (p. 22).

Acids and bases have a range of activities: some, including hydrochloric and sulfuric acids, sodium and potassium hydroxides, are very active even at ordinary temperatures, hence such acids and bases are unsafe to have around generally; others, including acetic acid and ammonium hydroxide, are much less active; still others, such as boric acid, are inactive. Carbohydrates, as a class of compounds, are inactive. The study of reactions involving acids, bases, and salts will receive considerable attention later.

Chemical stability has reference to the *tendency of the compound to decompose to make two or more other substances.* By way of examples: *water* is a very stable compound because it requires a very high temperature (about 2000° C.) for its decomposition to become appreciable; *carbon dioxide* is exceedingly stable since no one has ever yet been able to decompose it. *Mercuric oxide* is stable at ordinary temperatures but unstable at elevated temperatures (p. 16); *cane sugar* is likewise stable at ordinary temperatures but decomposes at such elevated temperatures as can be obtained easily in the laboratory or with the cook stove. *Hydrogen peroxide* is unstable even at ordinary temperatures, more so in the presence of sunlight, hence the advisability of keeping a reserve supply in a dark bottle and in a cool place.

It should be noted that in the light of above specifications, chemical *stability* cannot apply to simple substances (p. 26).

In the main, however, compounds which are met with in everyday concerns — water, carbon dioxide, those comprising the crust of the earth, those which are commonly used for various purposes — are stable at ordinary temperatures; as a consequence, our living concerns are thereby rendered more comfortable and less hazardous than would otherwise be the case.

Classification. Since approximately 275,000 compounds are already known with thousands more undoubtedly possible and yet to be discovered, it becomes a matter of considerable importance that they fall into relatively few classes from a chemical angle: namely, on a basis of common reacting tendencies. So it is that:

Of the thousands of compounds known:

↓	↓	↓	↓	↓	↓	↓	↓
Many are *Acids* which behave alike in chemical ways.	Many are *Bases* which exhibit common chemical behavior.	Very many are *Salts* with similar chemical behavior.	A few are *Metal oxides*	A few are *Nonmetal oxides*	Many are *Hydro-carbons*	Many are *Alcohols*	And so on for *other classes of compounds* some of which will be studied eventually

Thus the task of the chemistry student becomes tremendously simplified, since through the study of a few compounds which belong to the same class from the standpoint of their common chemical behavior, one is studying all compounds within this class in these respects. This is obviously an asset of considerable importance.

Naming of compounds. Many of the compounds of use today in everyday concerns, medicinally, and in the industries carry handed-down names given by our centuries-ago forebears. Some of these names, such as common salt, calomel, quicklime, and litharge, are not at all suggestive of contributing building materials. But, since the beginnings of chemistry science, chemists have aimed to devise a system of nomenclature for compounds which will suggest their element composition. For example:

The common or handed-down name	*The chemist's name*
Calomel	Mercur*ous* chlor*ide*
Corrosive sublimate	Mercur*ic* chlor*ide*
Common salt	Sodium chlor*ide*
Galena	Lead sulf*ide*
Litharge	Lead ox*ide*
Quicklime	Calcium ox*ide*
Slaked lime	Calcium *hydroxide*
Chalk Limestone	Calcium carbon*ate*
Borax	Sodium bor*ate*
Washing soda	Sodium carbon*ate*
Baking soda	Sodium hydrogen carbon*ate*
Saltpeter	Potassium nitr*ate*
Chili saltpeter	Sodium nitr*ate*
Lunar caustic	Silver nitr*ate*
Burnt alum	Potassium aluminium sulf*ate*

Significant name endings. Preliminary suggestions are next in order as to some *name endings* which have come to have significance in respect to chemistry nomenclature. Some of the endings to be stressed at this time have been presented incidentally on a previous occasion (p. 15) but a summary review is not amiss, as follows:

ide ending usually means that the compound is composed of *two elements.* An exception occurs in the naming of hydroxides such as sodium hydroxide and calcium hydroxide.

ate and *ite* as name endings signify the *presence of oxygen as one of three, or sometimes more, elements.* In a pair of compounds of the same three elements, with oxygen as one of them, the *ate compound* is the usually occurring one and it always contains a *larger weight proportion of oxygen than* does the corresponding *ite compound.* For example:

Sodium sulf*ate* 45.05% oxygen	Sodium sulf*ite* 38.08% oxygen
Potassium phosph*ate* 30.14% oxygen	Potassium phosph*ite* 24.45% oxygen

ic and *ous* are associated endings attached to the name of the first-mentioned element. The *ic compound* always contains a *higher weight proportion* of the second element, or group of elements, *than does the corresponding ous compound.* Thus:

Mercur*ic* chloride 26.11% chlorine	Mercur*ous* chloride 15% chlorine
Ferr*ic* sulfate 72.07% sulfate	Ferr*ous* sulfate 63.24% sulfate

ELEMENTS

And now for more information in regard to *elements* or *building materials:* where they are; how many are possessed by earth and in what comparative quantities; elements essential to the human body; classification possibilities; and their permanency.

Where are they? Since elements are the building materials for substances, simple substances and compounds, they must be present in earth's possessions wherever there are substances. Consequently, some are within that mixture of substances which comprises the atmosphere; portions of two of them are present within water; they are within all substances which earth's waters wash out from the air and lands; they are present within the mixtures of compounds that comprise plants and animals; but the greater portion of earth's elements are within the keeping of that vast conglomerate mass of hundreds of substances, mostly compounds, that make up earth's ball of solid matters.

In particular: earth's supply of *oxygen* element is distributed in oxygen substance and in carbon dioxide, both of which are chiefly in mixture in earth's atmosphere; in water wherever it may be; in most of the compounds that are components of earth's solid crust; and in most of the compounds comprising plants and animals. Supplies of *hydrogen* are distributed within water, and within carbohydrates and fats; but comparatively little is contained

within compounds which make up earth's crust. All of earth's supplies of *sodium, potassium, calcium,* and *chlorine* are present within compounds of these elements which are distributed in earth's crust or sea waters. Supplies of *carbon* are within the simple substance carbon of coal mixtures; in carbon dioxide of earth's atmosphere; in the calcium carbonate of chalk, marble, and limestone, which contribute to earth's solid crust; and in carbohydrates, fats, and proteins, which contribute to the mixture of substances comprising plants and animals. Earth's supply of the elements *gold, silver,* and *platinum* are almost entirely in the keeping of the simple substances gold, silver, and platinum scattered here and there in its solid portions.

How many elements? Ninety-two elements are claimed to have been discovered. About thirty elements receive common mention in connection with names of the simple substances or compounds which contain them; among such are barium, calcium, chlorine, magnesium, oxygen, silver, and zinc. The rest, or about sixty elements, including argon, lithium, molybdenum, selenium, silicon, and vanadium, are rarely mentioned save by the few people who have specific interest in them. (See table of elements on back cover of text.)

Relative quantities. To undertake an exact survey of the relative quantities of the various element materials possessed by earth — how much oxygen, iron, carbon, nitrogen, hydrogen, gold, etc. — relatively speaking, would be a colossal undertaking and perhaps impossible ever to achieve. Scientists can figure the relative quantities of element offerings provided within substances that make up the atmosphere, plant and animal mixtures, and within water; but up to the present time it has not been possible to ascertain the comparative element supply provided inclusively within substances throughout earth's tremendous ball of solid matters. Man's diggings, excavations, and minings have made but the merest scratches in earth's crust; furthermore, the solid matters thus revealed are but pigmy portions of that mixture of substances which, while they hold within their keeping the vast major portions of elements, have been buried for eons, and will continue to lie buried and hidden from man's investigations for more centuries or even eons to come, perhaps forever. Therefore, exact proportionate figures are seemingly out of the question.

Estimates, however, are possible and have been made as to the proportions of various elements provided inclusively within water, and within the substances that make up the atmosphere and the

outer layers of earth's crust. The following are some such computed findings: supposedly, the supply of the one element *oxygen*, distributed in these locations, is about equal to that of all other elements together, or approximately one-half the total; the next in proportionate quantity is the little heard of element *silicon*, which comprises about one-quarter of the total quantity of elements; then comes *aluminium* in quantity, relatively speaking; then *iron*. Computed comparative quantities of all other elements, within substances in the above specified locations, are as represented diagrammatically in the following:

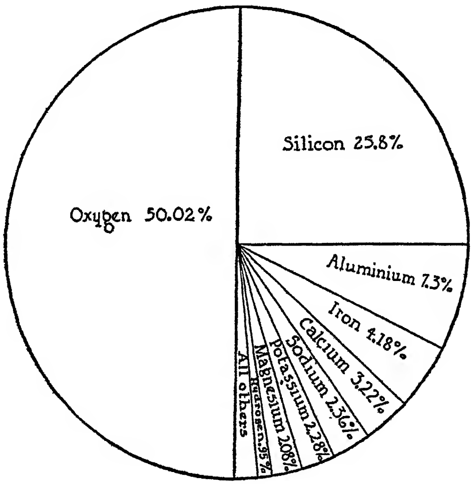


FIG. 11. The Approximate Element Composition of the Earth's Crust, its Oceans, and Atmosphere. (Clarke.)

There are some surprises in these figures. It is rather significant that such an overwhelming portion of earth's building materials is the one element oxygen; but this being true, it would seem to be the element most in demand by nature for building substances; and such is indeed the case, since most substances found already made in nature, and most that are made by man, do contain oxygen as one constituent element. It may be a surprise to find that there is so much silicon when we commonly hear no mention of it. The reason for this lies in the fact that the names which are used today for compounds containing silicon are the ones that have been used for centuries, having been given to them long before there was any knowledge of or interest in the element make-up of substances. Thus, quartz is the handed-down name for one widely distributed compound which contains silicon, clay

is another such compound, feldspar another, and mica is still another; and there are great quantities of these silicon compounds in earth's solid crust. Chemists, on the other hand, have devised names for these substances which do specify the presence of this element silicon, but these are not the names used by people commonly:

Common names	*Chemist's names*
Quartz	Silicon dioxide
Clay	Aluminium hydrogen silicate
Feldspar	Potassium aluminium silicate
Mica	Potassium aluminium hydrogen silicate

Elements essential to human body. The elements that are essential to the human body, and in what relative quantities, is a question of great importance. Of course *said elements are always for the purpose of contributing to substances that are essential for both body structure and other living needs.* As for the specific assortment of these elements and the proportionate quantities thereof, investigations to date by scientists who know how to carry out such studies have revealed the following requirements:

The elements	*Approximate percentages by weight*
Oxygen	65.0
Carbon	18.0
Hydrogen	10.0
Nitrogen	3.0
Calcium	2.2
Phosphorus	1.2
Potassium	.35
Sulfur	.25
Sodium	.15
Chlorine	.15
Magnesium	.05
Iron	.004
Manganese	.0003
Copper	.00015
Iodine	.00004
Other elements	Very small amounts

(Sherman: *Chemistry of Food and Nutrition,* 1941, Macmillan Company)

Accordingly, the sum total supply of some elements, for distribution within various requisite body compounds, is relatively large while that of other elements is exceedingly small. But the fact that some elements, notably iron and iodine, are required in such small quantities does not mean that substances containing them

are not important; they are, indeed, of great importance and quite as essential as those substances which, since they are made in relatively large quantities, obviously require their constituent elements in correspondingly large quantities. For example, the very *life* of the animal is dependent upon the presence of certain *iron* and *iodine* compounds; and its *health* is dependent upon the presence of these compounds in right quantities, small though these quantities be.

Must be in foods. It follows, then, that all elements required by the living, healthy body must be distributed within the various and sundry food substances that comprise the food intake. For most elements, such as *hydrogen, oxygen,* and *carbon,* it is not necessary to take thought as to whether one is or is not getting them in the daily food rations, because the average food mixture, selected even carelessly and without heed paid to body needs, contains these elements within the various food substances involved in more than sufficient quantities. Consequently, designated cells of the body take from various food substances brought to them such quantities of these elements as they require for building necessary quantities of their respectively required compounds; the rest of these elements get distributed in various stored or waste substances. With some elements, however, there is more uncertainty. For example: the *calcium* content of compounds of the food mixture, unintelligently or carelessly selected for the average daily portion, can easily be lacking in adequate quantities of this element for making sufficient calcium phosphate and calcium carbonate for bones and teeth and other calcium compounds for other essential uses. *Iron,* too, is quite likely to be present in insufficient quantities in compounds of an unconsidered diet, for the making within the body of such iron compounds and in such quantities as are normally required.

Classification of elements. A classification of elements after the manner about to be considered is not entirely satisfactory, but it has its helpful angles. The aim, therefore, must be to let this classification provide the help available and ignore the difficulties as far as possible. The basis for this classification is in respect to the *type of compound — namely, acid or base — to which the element contributes,* together with hydrogen and oxygen or with hydrogen alone. There are two varieties of elements after such specifications and they are called *metal elements* and *nonmetal elements.* (The elements hydrogen and oxygen are set aside and not classified in this connection as either metal or nonmetal elements.)

Metal elements. If the element in question as to classification can be found in combination with hydrogen and oxygen, and if the compound concerned is a base, then said *element is a metal element.* Here are examples:

A certain compound is composed of *sodium,* hydrogen and oxygen, the *compound is a base,* therefore, *sodium is a metal element.* Another compound contains the element *calcium* in combination with oxygen and hydrogen, this *compound is a base,* therefore, *calcium is a metal element.* After like reasonings:

Potassium Sodium Barium Calcium Magnesium Aluminium Zinc Iron Nickel Tin Lead Copper Mercury Silver Gold Platinum	are all *metal elements* because they occur in combination with oxygen and hydrogen *in compounds which are bases.*

Nonmetal elements. But if a given element is found in combination either with hydrogen or with hydrogen and oxygen, and if the compound thus involved is an acid, then said *element is a nonmetal.* For example:

There is a certain compound which is composed of hydrogen and *chlorine,* said compound is an *acid,* therefore, *chlorine must be a nonmetal element.* There are several compounds which are composed of hydrogen, *chlorine,* and oxygen, and all of these compounds are *acids;* hence in the light of these several more instances *chlorine,* again, is a *nonmetal element.* For another example, there are several compounds composed of hydrogen, *sulfur,* and oxygen; all of these compounds are *acids,* therefore, *sulfur* must be a *nonmetal element.* After similar reasonings:

Chlorine Bromine Iodine Sulfur Nitrogen Phosphorus Carbon	are *nonmetal elements* because they occur in combinations either with hydrogen or with hydrogen and oxygen *in compounds which are acids.*

Exceptions. Compounds composed of hydrogen and *nitrogen* or of hydrogen and *phosphorus* are not acids, neither are the many compounds of hydrogen and *carbon.* However, we are claiming for this classification only *some* degree of *helpfulness,* not exceptionless situations. After all, there are no classifications of any sort that are entirely unquestionable and completely satisfactory.

Metal and nonmetal elements versus metal and nonmetal substances. The student may be puzzled by the correspondence between this classification for elements and that of previous presentation (p. 28) in respect to simple substances; but the relationship is really a simple one in that metal substances are composed of the corresponding metal elements, while nonmetal substances are built of corresponding nonmetal elements. Thus: potassium, the metal substance, is composed of potassium, the metal element; sodium, the metal substance, is built of sodium, the metal element; chlorine, the nonmetal substance is built of chlorine, the nonmetal element; and sulfur, the nonmetal substance, is composed of sulfur, the nonmetal element.

Bases and acids. Incidentally, the foregoing classification of elements has provided an opportunity to gain some insight into the element make-up of bases and acids. Accordingly, if a compound is composed of a metal element together with oxygen and hydrogen, it is quite likely to be a base. But if a compound is composed of hydrogen and a nonmetal element, or of hydrogen together with a nonmetal element and oxygen, it is quite likely to be an acid. For example, and after consulting the lists of metal and nonmetal elements given on the previous page:

The compound containing the elements

$\left.\begin{array}{l}\textit{sodium}\\ \text{oxygen}\\ \text{hydrogen}\end{array}\right\}$ is a *base*, it is named sodium hydroxide.

$\left.\begin{array}{l}\textit{magnesium}\\ \text{oxygen}\\ \text{hydrogen}\end{array}\right\}$ is a *base*, it is named magnesium hydroxide.

$\left.\begin{array}{l}\textit{aluminium}\\ \text{oxygen}\\ \text{hydrogen}\end{array}\right\}$ is a *base*, it is named aluminium hydroxide.

$\left.\begin{array}{l}\text{hydrogen}\\ \textit{chlorine}\end{array}\right\}$ is an *acid*, one of its names is hydrogen chloride.

$\left.\begin{array}{l}\text{hydrogen}\\ \textit{bromine}\end{array}\right\}$ is an *acid*, one of its names is hydrogen bromide.

$\left.\begin{array}{l}\text{hydrogen}\\ \textit{iodine}\end{array}\right\}$ is an *acid*, one of its names is hydrogen iodide.

$\left.\begin{array}{l}\text{hydrogen}\\ \textit{sulfur}\end{array}\right\}$ is an *acid*, one of its names is hydrogen sulfide.

$\left.\begin{array}{l}\text{hydrogen}\\ \textit{chlorine}\\ \text{oxygen}\end{array}\right\}$ is an *acid*, one of its names is hydrogen chlorate.

$\left.\begin{array}{l}\text{hydrogen}\\ \textit{sulfur}\\ \text{oxygen}\end{array}\right\}$ is an *acid*, one of its names is hydrogen sulfate.

$\left.\begin{array}{l}\text{hydrogen}\\ \textit{phosphorus}\\ \text{oxygen}\end{array}\right\}$ is an *acid*, one of its names is hydrogen phosphate.

Permanency of earth's elements. By permanency of earth's elements is meant something like this: was earth presented in the beginning of its separate existence with definite quantities of its ninety-two element building materials; if so, have these elements always persisted in *exactly* these same quantities up to the present time; and will these specific quantities of said elements remain constant as in the beginning throughout all future time? Up to about forty years ago scientists believed that this was exactly the situation. It was believed, for instance, that earth originally came into possession of given quantities of oxygen, carbon, hydrogen, iron, etc., and that it would be impossible, ever, throughout all time, for nature to make an iota more or to destroy an iota of any one of these, earth's elements.

Some elements are disintegrating. But in 1896 a French scientist by the name of Henri Becquerel discovered that an element called *uranium*, which had been known to scientists for one hundred years, is very slowly disintegrating spontaneously; meaning by "spontaneously" that this disintegration takes place without any outside assistance, and that it cannot be encouraged or stopped by any means known to man. Then in 1898 M. and Mme. Curie succeeded in sorting out from residues of one ton of uranium ore exceedingly small quantities of the chloride and bromide of a new element which they found to be disintegrating one million times more rapidly than uranium; the name which they gave to this newly discovered element was *radium*. Since then certain elements of earlier discovery (palladium 1804, thorium 1828) and still other elements of more recent discovery (actinium 1899, radon 1900) have been found to be radioactive, that is, they are disintegrating spontaneously as are uranium and radium.

Two varieties of particles are ejected in the disintegration of all radioactive elements thus far discovered; they are called alpha particles and beta particles. *Alpha particles* upon ejection travel with a speed about one-tenth that of light; they are not very penetrating as to matter since their flight can be stopped by such obstacles as a sheet of paper or a very thin sheet of metal; they carry a positive charge of electricity. *Beta particles* travel ten times more rapidly than do alpha particles, hence with a speed which approximates that of light (186,000 miles per second); as a result, they are much more penetrating than are alpha particles and require thick sheets of metals to stop their flight; they carry a negative charge of electricity.

These particles are ejected in sequence: first alpha particles, then

beta particles, then alpha particles, and so on; but with each ejection, the exceedingly minute portion of the element from which the particles have been thrown gives way to another element. It follows, then, that with a series of ejected particles a series of new elements must be made — each from a portion of the immediately foregoing element — until an element is made which is not radioactive and the ejection of particles ceases. The radioactive sequence of elements during which radium is made and gives way in turn, but always only in part, to the next element is presented in the accompanying chart. This series, it will be observed, begins with uranium and ends with lead; which accounts for the fact that uranium ores always contain as components not only uranium compounds but radium compounds and lead. As for the alpha and beta particles, they get together in due time to make the element helium.

Uranium$_1$ ⟶ alpha particles
↓ 4.67×10^9 years
Uranium X_1 ⟶ beta particles
↓
Uranium X_2 ⟶ beta particles
↓
Uranium$_2$ ⟶ alpha particles
↓
Ionium ⟶ alpha particles
↓
Radium ⟶ alpha particles
↓ 1690 years
Radon ⟶ alpha particles
(Radium emanation)
↓ 3.85 days
Radium A ⟶ alpha particles
↓
Radium B ⟶ beta particles
↓ 26.8 minutes
Radium C ⟶ beta particles
↓
Radium C_1 ⟶ alpha particles
↓
Radium D ⟶ beta particles
↓
Radium E ⟶ beta particles
↓
Radium F ⟶ alpha particles
↓
Lead

Some elements are changing in quantity. So it is that supplies of some of earth's elements are changing as to their quantities: the supply of uranium is decreasing; that of radium is shifting in quantity since it is continuously being made and is continuously disintegrating; but the elements lead and helium are on the increase. As for radioactive elements, it would seem to follow from the above that the time should come eventually when their supplies would be utterly exhausted. But this is believed not to be the case since experimental investigations, to date, signify that at the end of a definite span of time, which differs for each element, only one-half of the quantity of element present at the beginning of said time will have disintegrated. Thus, with *radium* as the element and with the beginning quantity as *one gram* of this element — either within a radium compound, such as radium chloride, or within radium simple substance — it has been computed that:

in 1690 years $\frac{1}{2}$ gram of radium element will be left, the rest having disintegrated;
in another 1690 years $\frac{1}{2}$ of this remaining radium, or $\frac{1}{4}$ gram, will be left, the rest having disintegrated;
in another 1690 years $\frac{1}{2}$ of this $\frac{1}{4}$ gram of radium, or $\frac{1}{8}$ gram, will be left;
in another 1690 years $\frac{1}{2}$ of this $\frac{1}{8}$ gram of radium, or $\frac{1}{16}$ gram, will be left; etc.

Or, as the scientist puts it, *the half-life period* of radium is 1690 years. Therefore, although the time may come eons from now when very little of earth's radium is left, it can never disintegrate in its entirety. The radioactivity of uranium is only one-millionth that of radium, its half-life period being 4.67×10^9 years. Other radioactive elements have very brief half-life periods, that of radon or radium emanation being 3.85 days, that of radium B being 26.8 minutes.

Gamma rays. Another item of interest in connection with radioactive disintegration is that along with the ejection of alpha and beta particles, but chiefly with beta particles, a variety of energy is made, called *gamma rays,* which is after the order of energy called X-rays. Some of these "rays" have the same penetration as to matter as do the most penetrating of X-rays ("hard" X-rays), others have much greater penetration. Herein lies the reason why radium and radium emanation — from either of which elements *gamma rays* are continuously produced — and X-rays have similar therapeutic uses.

Radium emanation or radon, the element that follows immediately from radium, is incapable of remaining in combination with other elements, and it is gaseous. So, even though the radium element from which the radon is made may be combined within a radium compound, as it always is in nature, the radon, once made, drops any element or elements with which radium was previously in combination and travels along by itself. But, although gaseous, the radon usually remains occluded within the mass of the radium compound. It is for this reason that, eventually, it is lead substance instead of a lead compound that is present as a component of uranium, radium, and radon ore mixtures.

For therapeutic uses. Those who are acquainted with the therapeutic uses of radioactive elements know that sometimes radium is used and sometimes radium emanation or radon. The latter, as remarked above, usually remains occluded within the mass of the radium compound unless means are used for its separation. This can be accomplished either by heating the mixture, in which event the gaseous radon is automatically separated, or by dissolving the mixture in an acid solution, in which case the radon gas must be pumped off. The radon, thus separated, is collected in very thin glass tubes.

The radioactivity of radon is at a maximum about four hours after it is collected. It follows that for maximum therapeutic functioning, its useful life is brief.

Most elements are constant in quantity. Aside from lead and helium which are increasing slightly in their quantities, and the radioactive elements which are shifting slowly in their quantities but with a decreasing trend, other elements possessed by earth — and this means most elements — are believed to be fixed in their respective supplies.

Thus, it is believed that earth possesses definite quantities, respectively, of oxygen (p. 40), of hydrogen, of nitrogen, of sulfur, of sodium, and of most elements; and it seems probable that these quantities of these elements will remain thus fixed indefinitely throughout the future.

Questions

1. What is the experimental basis for the classification of substances as simple substances or compounds?

2. In reference to each of the following substances, tell whether you believe it to be a simple substance or a compound, and give convincing reasoning: nitrogen, mercuric oxide, water, platinum, iron rust.

3. Make a list of ten simple substances with which you are familiar outside of the laboratory. Give evidence of this familiarity. List several simple substances of your acquaintance not commonly encountered outside of laboratories. Describe them.

4. List some properties of the twelve metal substances that are tabulated on p. 29 for which properties are not already given.

5. To what does the term *physical state* refer? Should it be possible to obtain all simple substances in all three physical states? Give reason. Is it possible to obtain all compounds in all three physical states? Give example.

6. State the law of definite weight proportions. Give several examples. How is it possible to have two or more compounds that are composed of the same constituent elements? Give examples.

7. What differences in the composition of compounds within each of the following groups is indicated by their names:

   a. Hydrogen sulfide, hydrogen sulfate, and hydrogen sulfite?

   b. Mercurous chloride, mercuric chloride, and mercuric chlorate?

   c. Cupric oxide, cuprous oxide, and cupric hydroxide?

8. How many elements does earth possess? Where, in general, are these elements? Account for the fact that there are more simple substances than elements and illustrate by reference to specific examples.

9. What elements normally contribute to the composition of substances within the human body? Name at least ten of these elements in order of the relative weight proportions necessary for contributing to adequate quantities of substances for body needs. Of these elements, which are ordinarily supplied in adequate quantities within substances of the usual mixed diet? Which elements need to receive some special consideration in order to insure adequate quantities for making adequate amounts of substances containing them?

10. a. Name two radioactive elements. Why are they so classed?
    b. Tell something about each of the two varieties of particles which they eject; also tell something about gamma rays.
    c. What element is finally left in the ore mixture? What becomes of the two varieties of ejected particles?
    d. What is meant by "spontaneous disintegration" of these elements?
    e. Radium has a half-life period of 1690 years, radon a half-life period of 3.85 days. What does this mean?
    f. Why are radium and radon (radium emanation) kept within lead tubes?

CHAPTER IV

Oxygen the Element. Oxygen the Substance

OXYGEN ELEMENT

The element oxygen, meaning the building material, has been called to the attention a number of times. So now to summarize briefly items already stressed. As an *element,* oxygen is present wherever there are substances to which it is essential as a building material; it is the only element within oxygen substance and it is one of the elements within all oxygen compounds. Nearly one-half of the total of earth's supply of all elements is this one element oxygen. Moreover, although during the course of various reactions oxygen is continuously being taken from given substances to make other oxygen-containing substances, it seems probable that the quantity of this element possessed by earth, now, is a fixed quantity which will remain the same throughout all future time.

OXYGEN SUBSTANCE

Occurrence. Since oxygen, the substance, is gaseous, not only at ordinary temperatures but even at the very low temperatures that prevail in earth's coldest regions, *nearly all* of earth's supply of this substance is found where all substances that are gaseous are chiefly located: namely, in the air. Commonly about twenty-one per cent of the atmosphere's total volume is this one substance oxygen, a proportion that remains fairly constant. This constancy is due to the fact that, while oxygen is being removed continuously from the atmosphere both for respiration needs of animals and for various burning reactions, it is being made continuously, and as rapidly, in green portions of plants whence it passes into the atmosphere where stirring and mixing by breezes and air currents keep it in fairly even distribution. Word equations for some of these reactions are as follows:

Oxygen removed from air,

Hydrocarbons (of gasoline and fuel oil mixtures) + Oxygen → Carbon dioxide + Water
Carbon (of coal mixture) + Oxygen → Carbon dioxide
Glucose (within animal cells) + Oxygen → Carbon dioxide + Water

Oxygen returned to air (from chlorophyll cells of plants),

Carbon dioxide + Water → Oxygen + Plant carbohydrates

Also, because oxygen is slightly soluble, a *small portion* of earth's supply of this substance is in solution in the water of streams, ponds, lakes, and oceans. And this is fortunate, since fish must have this oxygen substance for living needs just as truly as do land animals, oxygen element which is combined within water itself being of no more use to them for respiration purposes than to land animals; in fact, fish "drown" in water which has an inadequate supply of oxygen substance in solution.

How long has it been known? Strange as it may seem, considering its vital importance and the fact that it is around us everywhere, conscious acquaintance with oxygen dates back to only a little over a century and a half ago. Historical records do show that longer ago than this two or three isolated men in their respective centuries had obtained knowledge of it, but what information they acquired in regard to this substance died with them.

From the writings of Leonardo da Vinci (1452–1519) it seems probable that he was aware of the gaseous substance in earth's atmosphere which we now call oxygen. John Mayow (1645–1697), an English physician, also recognized the presence of such a substance in the air but did not isolate it. Thus it came about that the discovery which was to bring the knowledge of oxygen to the world to stay and to grow to present-day magnitude was left for fairly recent accomplishment.

So, the final birthday of this substance — if one can thus label the time when something that has existed for eons became known to man — is definitely known to be August 1, 1774. It was on this day that Joseph Priestley — an Englishman, a dissenting preacher, and a more or less skillful scientist — happened to be heating what was then called *mercurius calcinatus per se* (now called mercuric oxide), and he obtained a gaseous substance which to his great surprise caused a candle which he chanced to thrust into it to "burn with a remarkably brilliant flame." [1] Thus did Priestley chance upon this substance which he felt convinced was different from all other gaseous substances known at that time. And he wrote of his discovery in a most interesting manner.

Later it became known that a Swedish contemporary, Karl Wilhelm Scheele (1742–1786), had really made this substance by three or four different methods prior to its independent discovery by Priestley, but the latter was the first to publish his findings.

[1] An interesting account of this discovery of oxygen is to be found in the *History of Chemistry* by F. J. Moore, McGraw-Hill Book Company, 1931, p. 46.

As should be expected, Priestley kept making more of this intriguing new substance, "dephlogisticated air" as he called it, in order to subject it to a variety of experimental investigations. Others likewise became interested in this substance; among them was Antoine Lavoisier, a distinguished French scientist, who, through his experiments with Priestley's "dephlogisticated air," accomplished more toward revealing its true nature than did Priestley himself. It was Lavoisier who discovered that the "new" gaseous substance really comprises twenty-one per cent of the atmosphere and who came eventually to recognize its relationship to everyday burning phenomena and to animal respiration. Also it was Lavoisier who gave to this newly discovered substance the name of *oxygen* which means *acid producer*, because he believed the element material therein to be the particular element essential to all acids; later findings proved that he was mistaken in that it is hydrogen element, not oxygen, that is thus essential. But the name *oxygen*, misnomer though it is, has persisted down through the years during which the searchlight of experimental investigations has revealed more and more concerning the properties of this illusive but important simple substance. And to this accumulated information we are now heirs.

Securing nearly "pure" oxygen. The dilute oxygen of the atmosphere is entirely sufficient for the everyday uses of people for respiration and burning. But when it comes to packing oxygen into tubes for man to take along as indispensable baggage for undersea and upper-air investigations, as well as for other uses, nearly "pure" oxygen is essential. Chemists and manufacturers, also, many times, need more concentrated supplies of oxygen than that of the air for their uses. So it has come about that the business of securing such supplies of oxygen has become one of the important industries of modern times.

For commercial uses. In obtaining almost pure oxygen in large quantities for commercial purposes, cost is obviously an important factor. But inasmuch as there is an already-made oxygen supply in the atmosphere, which is the manufacturer's for the taking, the expense of obtaining it undiluted from this source lies solely in the process. This involves sorting out oxygen, that is, separating it by physical means from its mixed association with other substances in the air, chiefly nitrogen, carbon dioxide, and water.

Without going into mechanical details concerning the process by which this is accomplished the main issues are as follows. First, the air is treated with certain chemicals for the removal of carbon

dioxide and water. Next, the remaining gaseous mixture of nitrogen and oxygen is subjected to a high pressure and increasingly lower temperatures until eventually (below − 196° C.) *liquid air* is obtained: namely, a mixture of liquid oxygen and liquid nitrogen (Fig. 12). Then, since the lower boiling-point liquid nitrogen is more volatile than the higher boiling-point oxygen, a slight raising

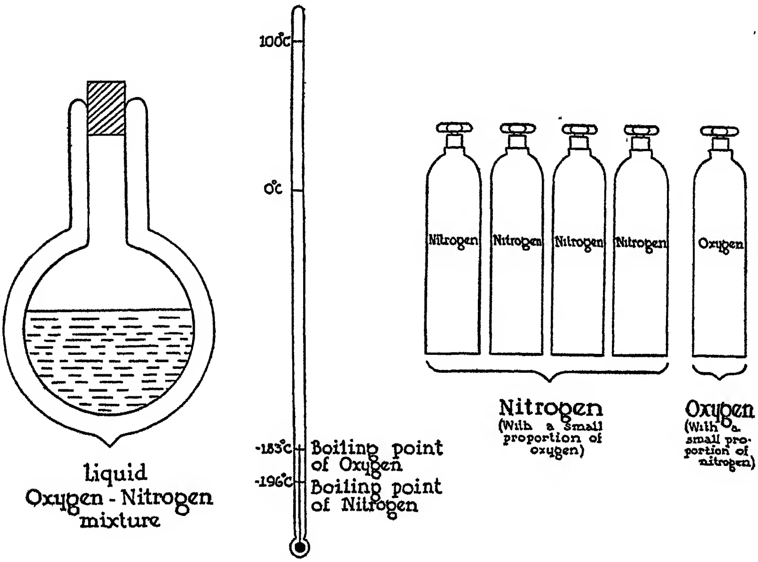


FIG. 12. Commercial Supplies of Oxygen Obtained from Air

of the temperature of the liquid air causes a more rapid evaporation of nitrogen which, in the gaseous state, is thus lifted up away from the oxygen. This nitrogen gas, mixed with small quantities of oxygen, is pumped into metal cylinders, packed there under pressure, sealed, and eventually finds a market for making ammonia (p. 63). Finally, with nitrogen nearly all separated, the temperature of the remaining liquid air is raised slightly until the oxygen (with a small proportion of nitrogen) begins to evaporate speedily, when it is collected just as was the nitrogen.

Incidentally, it is interesting to note that if these two gaseous substances are collected in tubes of the same volume and held therein at the same temperature and under the same pressure, *one tube of oxygen* is obtained for every *four tubes of nitrogen*, which corresponds to their volume relationship in the air (Fig. 12).

The uses for which these supplies of nearly pure oxygen are purchased play an indispensable part in the promotion of various

present-day world enterprises. Some of these uses will receive attention in a later chapter (pp. 77–83).

Other sources of oxygen. Since oxygen of air mixture is the only supply of this substance already made, other sources than from air must necessitate making it from oxygen element provided in oxygen-containing compounds. There are thousands of oxygen compounds and all of them can be considered as potential possibilities for the making of oxygen substance. Actually, however, many compounds, including carbon dioxide, carbohydrates, and calcium carbonate, have never been known to yield up their oxygen element toward this end. But there are other oxygen-containing compounds from which oxygen substance can be made more or less readily. *Water* would seem to be the obvious first choice for this purpose; and it is true that when an electric current is passed through water, to which a little acid has been added, the water is indirectly coaxed into yielding up its oxygen and hydrogen elements for the making of the two simple substances oxygen and hydrogen (Fig. 13) after the reaction represented thus:

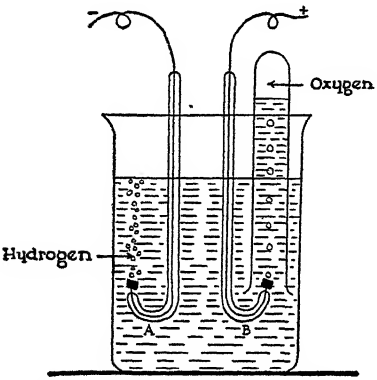


FIG. 13. Oxygen Made by the Decomposition of Water

$$\text{Water} \rightarrow \text{Oxygen} + \text{Hydrogen}$$

Inasmuch as water can be obtained without cost, this would seem a feasible method for making commercial supplies of oxygen, and this method was indeed used before inexpensive means were devised for securing the low temperatures that are required for separating oxygen from air mixture. But nowadays the cost of securing these low temperatures is less than that of the electricity necessary for making oxygen from water.

We have already heard that Priestley made oxygen by decomposing what was at that time called *mercurius calcinatus per se*, now called *mercuric oxide*. The reaction is easily accomplished as follows:

A small quantity of *mercuric oxide* is put into a test tube and heated (Fig. 1). When its temperature is high enough, decomposition of the mercuric oxide begins to take place, *very slowly*, as evidenced by the gradual making (1) of

mercury substance which, although gaseous at the high temperature at which it is made, presently condenses to liquid mercury on cool portions of the tube where it collects in characteristic silvery droplets; (2) of oxygen whose presence, while not sensed directly, can be detected by thrusting into it a "glowing" wood splint which, though it burns only with "glowing speed" with the dilute oxygen of the air, springs into vigorous burning when surrounded by the greater concentration of oxygen within the tube. The word equation which represents this reaction is as follows:

Mercuric oxide → Oxygen + Mercury

But this method for making oxygen is of more interest historically than from a practical viewpoint since mercuric oxide is expensive and the yield per pound is comparatively small (p. 56).

So much for two oxygen compounds which under right conditions lend themselves to the making of oxygen substance. We might consider several other such possibilities but we shall satisfy ourselves with only two, selected because of their classic significance and their adaptability to the easy making of such small quantities of oxygen as are commonly needed for its laboratory study. These two compounds are *potassium chlorate* and *manganese dioxide* and the procedures for making oxygen from them are described in some detail as follows:

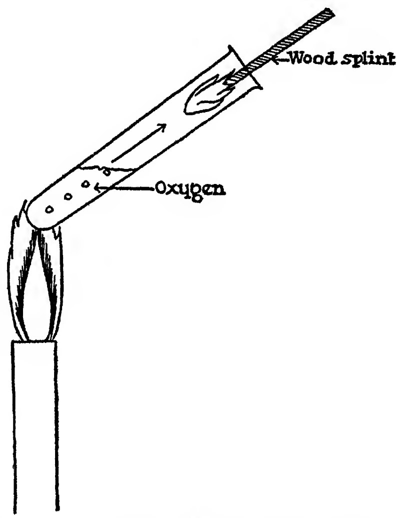


FIG. 14. Oxygen Made by the Decomposition of Potassium Chlorate

Oxygen made from potassium chlorate. When this compound — white, crystalline, solid — is put into a test tube and heated (Fig. 14) it melts (at about 368° C.) before decomposition becomes appreciable. But as heating is continued and the liquid potassium chlorate boils (about 400° C.) reaction begins to take place so rapidly that there is need for very careful control of oxygen-making through intelligent adjustment of the heat applied. With uncontrolled technic the reaction can easily become uncomfortably, even dangerously, violent. The other product of the reaction is potassium chloride, a colorless compound which is liquid at the high temperature at which it is made but solid at ordinary temperatures.

Potassium chlorate → Oxygen + Potassium chloride

Oxygen made from manganese dioxide. Manganese dioxide, a black solid, can be made to decompose after the same procedure as that used with potassium chlorate (Fig. 15). But making oxygen from this compound is more difficult than from potassium chlorate because manganese dioxide must be at a much higher temperature (about 535° C.) before it begins to give up appreciable quantities of its oxygen element, and even then gives it up very sluggishly, and only part of it at that. Consequently, along with oxygen, there is made another manganese oxide — brown in color — which contains a lower percentage of oxygen element than does the initial black manganese dioxide.

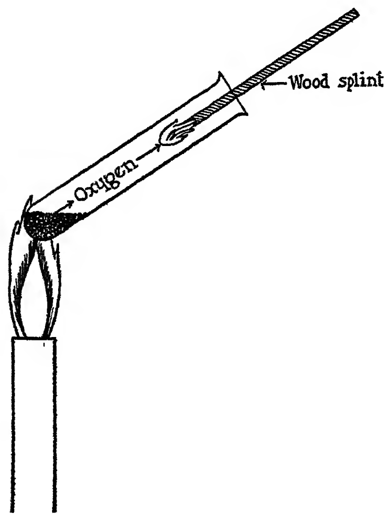


FIG. 15. Oxygen Made by the Decomposition of Manganese Dioxide

A comparison of the foregoing. Of the last three means presented for making oxygen, that from potassium chlorate is obviously the most feasible, first because this compound decomposes appreciably at a lower, hence a more easily obtained, temperature than does either mercuric oxide or manganese dioxide; second, because larger quantities of oxygen are made therefrom:

From one pound	*Oxygen made*
Mercuric oxide	.074 lb.
Potassium chlorate	.393 lb.
Manganese dioxide	.122 lb.

And now, with a let-us-see-what-will-happen attitude, for an experimental venture which has come to be a classic: namely, that of mixing potassium chlorate and manganese dioxide and heating the same, a venture which may very likely have been prompted the first time it was chanced upon by just such a lively curiosity motive. And so, ostensibly just for the fun of it:

Take some *potassium chlorate*, mix a little *manganese dioxide* with it quite thoroughly, put the mixture into a test tube and heat it (Fig. 16). And almost right away, certainly at a much, much lower temperature than that at which manganese dioxide decomposes, even considerably below that at which potassium chlorate melts, oxygen begins to be made and so rapidly that the heat supply must be very carefully controlled in order to avoid too violent delivery of this gaseous substance.

Certainly this seems an astounding happening: that oxygen should be thus made at a temperature far below that at which it can be made from either one of these compounds alone. It is not surprising, therefore, that this mixture has come to have an important place in general laboratory student practice as a source of small and easily obtainable supplies of oxygen.

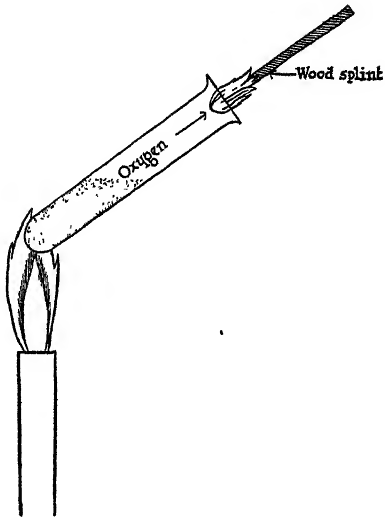


FIG. 16. Oxygen from Potassium Chlorate—Manganese Dioxide Mixture

But for thinking students, a question will be forthcoming: namely, is the oxygen made from potassium chlorate, or from manganese dioxide, or from both? An answer to this question has come as a result of many experimental studies of this phenomenon from a quantitative angle; and always, when such studies have been made with painstaking accuracy, it has been found that back in the test tube, when reaction is complete, the substances left are potassium chlor*ide* and *manganese dioxide*, and that the quantity of manganese dioxide is *exactly equal* to the quantity present before any reaction began! (Fig. 17.)

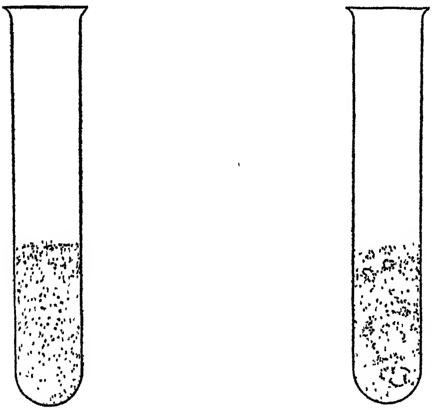


FIG. 17

A. If in the beginning the mixture contains 5 grams of potassium chlor*ate*, *2* grams of manganese dioxide,

B. When the reaction is complete, there will be left within the test tube 3.04 grams of potassium chlor*ide*, *2* grams of manganese dioxide.

It appears evident, then, that under these circumstances oxygen is made from potassium chlorate, manganese dioxide seeming not to enter into the reaction at all.

What, then, is the function of the manganese dioxide? And the answer

to this question leads to one of the most interesting and least understood of chemical phenomena: namely, that the *speed of a chemical reaction can be affected, that is, increased or decreased, by the mere presence of some selected substance which in itself is seemingly not part of the reaction.* Such substances have received various labels: *catalytic agents*, or *catalysts*, or *contact agents*. Thus, manganese dioxide functions as a catalyst for the decomposition of potassium chlorate, in that, by its mere presence, this reaction takes place more speedily. One method for representing the presence of this catalyst in respect to this reaction is as follows:

$$\text{Potassium chlorate} \xrightarrow{\text{manganese dioxide}} \text{Oxygen} + \text{Potassium chloride}$$

Questions

1. Make a statement in which you differentiate clearly between oxygen the element and oxygen the substance.

2. Where is oxygen element located? About how much does earth possess comparatively speaking? Where is oxygen substance to be found in earth's matter possessions?

3. How long has the substance oxygen been known? What famous scientists were associated with (a) the final discovery and (b) the later study of oxygen?

4. From what source are commercial supplies of oxygen obtained and by what method? Is the process involved physical or chemical? Why?

5. What substances, in general, can be considered as potential sources from which oxygen substance can be made? Name at least three compounds from which oxygen can be made in the laboratory. Assemble word equations for the reactions concerned. Which of the methods studied appears to you to be the most practical for securing such quantities of oxygen as are needed for laboratory use? Give reasons for your selection.

6. When potassium chlorate and manganese dioxide mixture is used for obtaining oxygen: (a) What is the function of the potassium chlorate? (b) What is the function of the manganese dioxide? (c) What name is given to a substance which functions as manganese dioxide does in respect to this reaction?

CHAPTER V

Catalytic Agents

With the foregoing introduction to the functioning of these wonder-working substances or *catalysts,* we have met with a subject which is worthy of further detailed attention. For this purpose we shall interrupt the study of oxygen for the time being.

Catalytic agents. The definition of a catalytic agent or catalyst has virtually been given (p. 58), but let it be said again that *a catalytic agent is a substance which, by its mere presence, affects the speed of a chemical reaction without itself seemingly becoming otherwise involved.* There has been limited knowledge of the functioning of selected substances as speeding-up or speeding-down agents in respect to chemical reactions since the early 1800's, but chemists did not become seriously interested in this extraordinary speed factor until about one hundred years later. However, since the early 1900's intensive studies of this phenomenon have been made with the result that, today, catalysis constitutes one of the major divisions of chemistry investigations. And, as should be anticipated, these studies have invaded many fields of human interest some of the findings of which will be the concern of the rest of this chapter.

Catalysts included in recipes for food preparations. It is known now that since ancient times people have been including substances which function as catalysts for reactions concerned as part of recipe procedures toward securing desired products. The following are examples.

In making leavened bread. For centuries, recipes for leavened bread have called for the inclusion of yeast among materials used and for keeping the dough mass in a warm place. But no one knew in the long ago days — most people do not know now — either why yeast is necessary, or why the bread dough must be kept warm; they simply knew that if these directions were observed bread dough would "rise"; if not observed the dough would not "rise." So it was left for chemists to find out that in leavening bread several reactions take place:

First, *starch* (in flour) reacts with *water* to make *maltose.*
Second, *maltose* reacts with *water* to make *glucose.*
Third, *glucose* decomposes to make *carbon dioxide* and *grain alcohol.*

Moreover, chemists have also learned that not one of these reactions will proceed with appreciable speed until (1) the dough mass is warmed, when a catalyst, called an amylase, is developed from a component of the flour for speeding up the first reaction, and (2) bread yeast is introduced which provides two catalysts, called maltase and zymase, for speeding up the other two reactions. As a result, when these three catalysts are obtained in the bread dough mixture the aforementioned reactions follow upon each other with appreciable speed. Word equations for these reactions, together with the respective catalysts concerned, are as follows:

$$\text{Starch} + \text{Water} \xrightarrow{\text{amylase}} \text{Maltose}$$

$$\text{Maltose} + \text{Water} \xrightarrow{\text{maltase}} \text{Glucose}$$

$$\text{Glucose} \xrightarrow{\text{zymase}} \text{Carbon dioxide} + \text{Grain alcohol}$$

The "rising" of bread is, of course, due to gaseous carbon dioxide which, on its way out, leaves a porous dough mass. When sufficient carbon dioxide has been made to give the mass a desired degree of "lightness" the dough is moulded into loaves and all catalysts are presently destroyed by the heat of the oven.

In cheese-making. Among recipes for various cheese-makings that have been handed down from centuries of usage is one for making cheese from cow's milk which in olden days called for the inclusion, among other materials, of ground-up lining of calf's stomach. The origin of this recipe is so ancient and obscure as to be legendary, actual knowledge of the reactions concerned being less than one hundred years old. But it is claimed now that, in the process of cheese-making, a protein of milk mixture, called *caseinogen,* reacts with *water* to make the protein of cheese, called *casein.* Nonetheless this reaction is negligible in speed save in the presence of a favoring catalyst; and one such catalyst, named *rennin,* is made in abundance within the mucosa of the stomach of the calf:

$$\text{Caseinogen} + \text{Water} \xrightarrow{\text{rennin}} \text{Casein}$$

In this manner is explained the inclusion in the old cheese-making recipe of this mucosa in finely divided form. In these modern days, means have been devised for extracting the rennin; as a result, the traditional recipe has been modified to include this extract rather than the entire powdered mucosa.

In making candy and frosting. The making of "boiled" candies and "boiled" frosting, although possibly not of such ancient practice as the making of bread and cheese, provides another

example of a handed-down recipe which includes what seems to be a catalyst.

Both processes necessitate a reaction between cane sugar and water to make glucose and fructose, which in itself is very slow even at the prolonged high temperature of the long-boiling period; but if a little acid is introduced the length of time necessary for completion of the reaction is considerably shortened, and it may be that the acid functions as a catalyst:

$$\text{Sucrose} + \text{Water} \xrightarrow{\text{acid}} \text{Glucose} + \text{Fructose}$$

Any acid will function in this manner, but in food preparation either acetic or tartaric acid is obviously a better choice than such an acid as hydrochloric acid.

Investigation of these inherited recipes is interesting, and there are others of long usage which could be made more meaningful in similar manner. But let us get on to more modern concerns which involve tales of catalytic agents.

Catalysts and modern industries. The tremendous progress that has been made during the past thirty-five years in the field of manufacturing has, to a surprising degree, become possible only through the agency of catalysts. Some industries have been born, others have been revolutionized, due to the conscious searching for and ultimate discovery of functioning catalysts for speeding up key reactions which, without such aid, would proceed too sluggishly to yield desired products on a sufficiently large scale for practical commercial uses. The following are instances in this connection.

Sulfuric acid manufacture. Our first story has to do with the making of sulfuric acid which is the most important chemical of industry, because, in one way or another, it is used in the manufacture of more useful materials — fertilizers, explosives, rayon, artificial leathers and woods, lacquers and paints, drugs, dyes, soaps, paper, glass, steel, etc. — than any other one substance.

Now sulfuric acid has been made on a commercial scale for nearly two hundred years. However, until the early 1900's it was manufactured almost entirely by a process — called the Lead Chamber Process — which yields an impure and dilute product. But there are many materials, such as explosives, celluloid, and rayon, in the manufacture of which "pure" and concentrated sulfuric acid must be employed. As a result, the time came, about the beginning of the present century, when the need for a better grade of this acid became urgent. Attempts were made to purify and concentrate the product of the Lead Chamber Process but they were

far from successful. The alternative was to search for another method for making this essential substance.

Already a good start had been made toward this end. It had been known for nearly a hundred years that a good grade of concentrated sulfuric acid was possible from a sequence of two reactions as follows:

Sulfur dioxide + Oxygen → Sulfur trioxide
Sulfur trioxide + Water → Sulfuric acid

And a catalyst had been discovered, too, namely platinum, for speeding up the first of these reactions which, without such aid, is exceedingly slow. The second reaction is in no need of such accelerating assistance. But trouble had been encountered in the use of this catalyst. It was found that when platinum was introduced into contact with sulfur dioxide and oxygen it would catalyze the reaction for a time, then would gradually become "poisoned": meaning that, although present, for some unknown reason its function was interfered with.

Thus far had this information of nearly a century before carried, and there the matter rested until the end of the 1800's when interested chemists resurrected these ancient findings and set themselves to the task of discovering what was responsible for "poisoning" the platinum catalyst, and how to circumvent it. A long story is involved with these searchings but, eventually, the information sought was obtained and the way paved for the development of a rival of the Lead Chamber Process, which came to be called the Contact Process, for the making of this important acid; and, as was so greatly desired, the product was found to be of an excellent grade.

Of course, platinum is very costly, but it must be remembered that, as a catalyst, it is not destroyed in the reaction, hence can function over and over again for catalyzing reactions of large quantities of substances concerned.

It is this more concentrated, purer, and less expensive sulfuric acid that has been one of the contributing factors in the development to present-day proportions of some of our largest modern industries. And it was the not-so-long-ago discovery of how to render a catalyst effective in speeding up to practicable proportions an otherwise valueless reaction, which is at the root of this important chain of industrial events.

For making nitrates. The next tale has to do with the tremendous development during the *past* thirty years of the *fertilizer* and

high explosive industries. Fertilizers and explosives are obviously desired for vastly different uses, but one of the food needs of plants is the same as one of the manufacturer's needs for explosives: plants need nitrate from which they are equipped to take nitrogen for building into their proteins; the manufacturer needs nitrate for making high explosives.

Before the 1900's this need for *nitrate* on the part of *plants* had been partially met by various means as follows. (1) Animal manures were spread on soils and such excreta contain nitrogen compounds from which, through the agency of certain bacteria in soils, nitrates are made. (2) Guano, with its component of Chili saltpeter or sodium nitrate, was brought by shiploads from the west coast of South America, and within this compound, as the name implies, the nitrate is already present. (3) Fields were enriched by growing crops of clover or other leguminous plants whose root nodules house certain bacteria which are able to utilize gaseous nitrogen of the atmosphere, together with other substances at hand, for making this essential nitrate in exactly the location where needed: at the very roots of the needy plants.

But, despite these sources, there was not sufficient nitrate to maintain the fertility of incessantly cultivated lands. Accordingly, by the late 1800's, certain scientists of Europe, with an eye to the future, had begun to feel some concern about the matter. And to add to the worries, it seemed inevitable that one of these nitrate supplies, that of guano, would in due time become exhausted.

Thus, for the sake of the future food supply of the world, as well as for other needs, the problem was put up to the chemist of seeing if something could be done about making nitrate right at home from the ever ready nitrogen supply of the air.

And so again, as when confronted with the problem of making sulfuric acid, it happened that certain beginning information was already at hand, since it was already known that:

Nitrogen reacts with *hydrogen* to make *ammonia* (nitrogen hydride).
Ammonia reacts with *oxygen* to make *nitric acid* (or hydrogen *nitrite*) and water.

Yet, while this information was good as far as it went, the fact remained that, unaided, these reactions proceed very, very slowly. So researches were begun for ways for speeding them up sufficiently to render them useful; and naturally these investigations included a hunt for catalysts.

The rest of the story can be anticipated. In due time — about 1900 — a German chemist by the name of Fritz Haber discovered

that uranium acts as a catalyst (other catalysts have been discovered since) for the making of ammonia after the above-mentioned reaction; and about that same time another German chemist, Wilhelm Ostwald, discovered that platinum functions as a catalyst for speeding up the second reaction, or the reaction whereby nitric acid can be made from ammonia. And once nitric acid is obtained, the making of all other nitrates is accomplished very easily.

Following upon these findings, means for financing the production of synthetic nitrates on a large scale were obtained by 1904; and by 1915 Germany had developed this industry to such an extent that she was able to manufacture nitrates, for use as fertilizers and in making high explosives, not only in sufficient quantities to render her independent of the Chili saltpeter deposits but to sell to other countries.

During the years since then, manufacturers in most, if not all, other countries have learned how to make nitrates either after the Haber process or after some other method, until today the synthetic nitrate industry is a worrisome competitor to the Chili saltpeter industry: worrisome, that is, to those whose financial interests are concerned with the latter.[1]

Hydrogenation of fats. Fats have two world-wide uses, namely, for food and for the making of soap. For both of these uses, solid fats are and always have been generally preferred. However, up to about thirty-five years ago there were not enough solid fats to meet the food requirement of the world's peoples and to make sufficient soap for cleansing purposes the world over. And, quite significantly, this great deficiency of solid fats was in the face of a considerable excess of fats of the liquid variety, such as cottonseed oil and other plant fats and those of fish oils; hence these fats, not being generally desirable, were to quite an extent utter waste.

Now it had long been known that, from a composition angle, solid fats simply contain a slightly higher weight proportion of hydrogen than do liquid fats:

A typical *solid* fat, weight proportion between
carbon, hydrogen, and oxygen is 684 : 110 : 96

A typical *liquid* fat, weight proportion between
carbon, hydrogen, and oxygen is 684 : 104 : 96

Hence, chemists became convinced that if only a less desirable liquid fat could be made to combine with hydrogen a fat of the solid variety should result:

[1] At present (1943) there is a federal limitation on the sale of nitrate fertilizers in order to conserve nitrates for war industries.

$$\overbrace{\begin{array}{c}\text{carbon : hydrogen : oxygen}\\ 684 : 104 : 96\end{array}}^{\text{Liquid fat}} + \begin{array}{c}\text{Hydrogen}\\ \text{6 parts}\\ \text{by weight}\end{array} \longrightarrow \overbrace{\begin{array}{c}\text{carbon : hydrogen : oxygen}\\ 684 : 110 : 96\end{array}}^{\text{Solid fat}}$$

But repeated trials to bring about this combination revealed the fact that an exceedingly sluggish reaction was involved.

So here was another reaction of great potentiality, but where was a substance that would catalyze it! Therefore, the searching began; and in 1899 a French scientist, Paul Sabatier by name, discovered that nickel functions in this capacity:

$$\text{Liquid fat} + \text{Hydrogen} \xrightarrow{\text{nickel}} \text{Solid fat}$$

Very simple this seems, but the discovery was of tremendous importance and Sabatier was awarded the much coveted Nobel prize for his achievement.

Thus did the discovery of a catalyst for an otherwise useless reaction lead to the creation of an entirely new industry: the so-called hydrogenation of fats. Today the better grades of cottonseed oil are hydrogenated to make lard substitutes, while poorer grades of plant fats, as well as other less desirable liquid fats, such as fish fats, are hydrogenated to make semisolid fats which are used in the manufacture of laundry soaps. Other and more effective catalysts than nickel have since been discovered to speed up combination between liquid fats and hydrogen, but they are secrets of the manufacturers concerned.

It would be possible to continue with other tales that would bear evidence, as do the foregoing, of the amazing differences that discovered catalysts for otherwise useless reactions have wrought already in the manufacturing concerns of the world. The potentialities of other yet-to-be discovered catalysts for other slow but potentially useful reactions can only be guessed at, but the guess has a note of magic.

Nature has always been using catalysts. Finally, in respect to this subject of catalytic agents, it has been found that nature has been using them always, in some instances to speed up reactions which, as far as man is concerned, are a nuisance, in other instances to control speeds of reactions which are of vital importance.

Water as a catalyst for some reactions. It is now believed that *wet* iron rusts because water acts as a catalytic agent for favoring the reaction between iron with oxygen:

$$\text{Iron} + \text{Oxygen} \xrightarrow{\text{water}} \text{Iron oxide}$$

Likewise it is believed that moist peas, beans, and all protein-containing foods spoil within a short time because the water present is a catalyst for speeding up certain reactions which are responsible for their "spoilage." As a result, *dry* iron does not rust appreciably because a catalyst for the reaction is absent; and in the preservation of foodstuffs by drying one is simply removing a catalyst for reactions which, without said catalyst, take place very slowly.

Catalysts and vital concerns. From a vital angle, it now seems certain that down through eons of time, ever since there has been life upon the globe, nature has always been using catalysts within plants and animals as control agents for various and sundry reactions that are essential to their healthy living.

Essential to plant life. By way of one example in respect to plants, that reaction of primary importance which takes place within the cells of green plants, whereby carbon dioxide and water react to make oxygen and plant carbohydrate, would be negligible in speed if chlorophyll were not provided to function as a catalyst:

$$\text{Carbon dioxide} + \text{Water} \xrightarrow{\text{chlorophyll}} \text{Oxygen} + \text{Carbohydrate}$$

Essential to animal life. As for humans, nature makes various catalysts in specific locations and sees to it that they are provided at the right times and at the right stations, all along the digestive tract from the mouth to the large intestine, for speeding up digestive reactions. The following are word equations for these reactions with their specific catalytic agents:

In salivary digestion

$$\text{Starches} + \text{Water} \xrightarrow{\text{ptyalin}} \text{Dextrins} + \text{Maltose}$$

In gastric digestion

$$\text{Proteins} + \text{Water} \xrightarrow{\text{pepsin}} \text{Proteoses} + \text{Peptones}$$

In intestinal digestion

$$\text{Dextrins} + \text{Water} \xrightarrow{\text{amylase}} \text{Maltose}$$

$$\text{Starches} + \text{Water} \xrightarrow{\text{amylase}} \text{Maltose}$$

$$\text{Maltose} + \text{Water} \xrightarrow{\text{maltase}} \text{Glucose}$$

$$\text{Sucrose (cane sugar)} + \text{Water} \xrightarrow{\text{sucrase}} \text{Glucose} + \text{Fructose}$$

$$\text{Lactose (milk sugar)} + \text{Water} \xrightarrow{\text{lactase}} \text{Glucose} + \text{Galactose}$$

$$\text{Proteins} + \text{Water} \xrightarrow{\text{trypsin}} \text{Peptids}$$

$$\text{Proteoses} + \text{Water} \xrightarrow{\text{trypsin}} \text{Peptids}$$

$$\text{Peptones} + \text{Water} \xrightarrow{\text{trypsin}} \text{Peptids}$$

$$\text{Peptids} + \text{Water} \xrightarrow{\text{crepsin}} \text{Amino acids}$$

$$\text{Fats} + \text{Water} \xrightarrow{\text{steapsin}} \text{Fatty acids} + \text{Glycerol}$$

But some students may say: "We know about these agents, for they are enzymes!" And so they are, but they are catalytic agents, too, since *enzymes are catalytic agents which are made within the cells of animals and plants.*

More is known about these digestive reactions than about reactions that take place within cells, because access to the alimentary tract is more easily attainable than to the cells. But it is suggested that insulin may be a catalyst which functions at some stage in the series of reactions involved in the metabolism of glucose. It is also claimed that thyroxine and adrenalin may be provided to catalyze other reactions concerning which there is less certainty. Indeed, it is probable that many reactions within the cells are controlled — speeded up or speeded down — by the presence of specific catalysts provided for such purpose.

Catalysts for speeding-down reactions. Although catalysts which increase speed of chemical reactions are in the greater demand, it is sometimes desirable to decrease speed of reactions by such means. For example: the life of unstable hydrogen peroxide would be exceedingly transient if the manufacturer did not introduce a catalyst to delay its decomposition, and a little strong acid or a little phenacetin functions in this capacity:

$$\text{Hydrogen peroxide} \xrightarrow{\text{phenacetin}} \text{Oxygen} + \text{Water}$$

Of vital importance is the probability that negative catalysts, as such are sometimes called, are made in the cells of plants and animals for checking reactions concerned when so desired.

Questions

1. In general, what is the function of a catalyst? Illustrate by reference to a specific catalyzed reaction of your own experience.
2. What is the function of yeast when included in a recipe for bread-making? Give details.
3. Give word equations for reactions involved in each of the following commercial processes, indicating functioning catalysts where such are necessary:
   a. Making sulfuric acid by the contact method.
   b. Making of nitrate.
   c. Hydrogenation of fats.

Name some industrial developments which have become possible as a result of these commercial processes. Consider what, if any, effects these developments have had in relation to your concerns.

4. What precaution should be observed in the care of steel instruments or other iron equipment in order to prevent their rusting? Give reason.

5. Why is it possible to store dried milk for long periods, whereas fresh milk spoils in a relatively short time? Mention other examples of food preservation to which the same principle applies.

6. What are enzymes? Why are they included among catalysts?

7. In regard to digestive reactions presented in this chapter what chemical reactions are involved? Specify a functioning enzyme for each reaction. What is the function of these enzymes?

CHAPTER VI

Oxygen the Substance (*continued*)

Making and collecting oxygen for laboratory study. Before the subject of oxygen was set aside for that of catalytic agents, it had already been found that a feasible method for making supplies of this simple substance (p. 57) for laboratory study is through the decomposition of potassium chlorate with an admixture of manganese dioxide as a catalyst for the reaction. The generator:

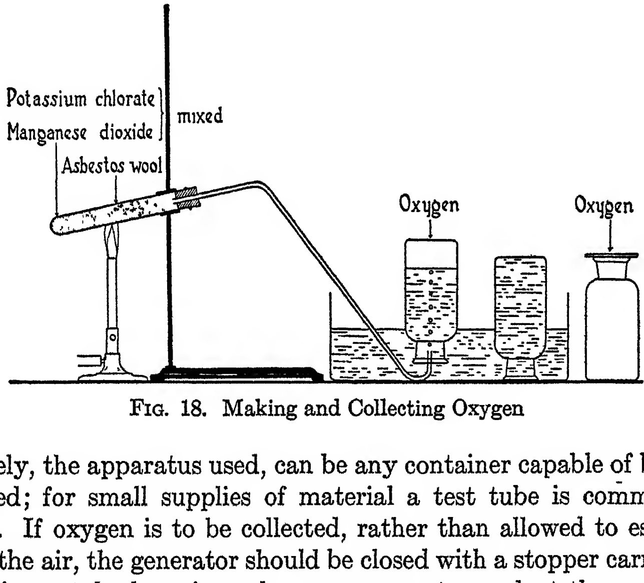


FIG. 18. Making and Collecting Oxygen

namely, the apparatus used, can be any container capable of being heated; for small supplies of material a test tube is commonly used. If oxygen is to be collected, rather than allowed to escape into the air, the generator should be closed with a stopper carrying a delivery tube bent in such a manner as to conduct the gaseous oxygen down through a cistern of water and up into the neck of a water-filled collecting bottle. An arrangement that is frequently employed is pictured above (Fig. 18) and some details of operation are given as follows:

The potassium chlorate (⅔) and manganese dioxide (⅓) are well mixed before being introduced into the test tube carrying the delivery tube. The test tube is clamped to a support in such a position as to provide both for easy heat control of the mixture and for easy collection of the oxygen. The col-

lecting bottles should be made ready in advance for their part in the performance by filling each in turn to the brim with water, slipping a glass plate over the mouth of the bottle and inverting it in the cistern of water.

When all is ready for the operation the mixture is heated *gently;* then when sufficient oxygen has been made to displace all air in the generator and delivery tube, the latter should be inserted into the neck of the first collecting bottle; the oxygen will rise through the water which at the same time is pushed down out of the bottle into the cistern. (Why?) Obviously, when the bottle is empty of water it is full of oxygen, at which time the bottle of oxygen can be removed by slipping a glass plate down through the water and over the mouth of the bottle, which can then be removed and placed with mouth up but still covered. As many bottles of oxygen as are desired can be collected after this manner.

There are incidental items in regard to good technic on the part of this piece of experimentation which are worthy of note. (1) The oxygen should be made first from top layers of potassium chlorate of the mixture (why?); then as each layer of potassium chlorate is decomposed the heat can be carried down to successive lower layers. (2) The speed of making oxygen is dependent on the quantity of heat provided and is, therefore, absolutely under the control of the operator: too rapid heating is accompanied by too rapid making of oxygen and vice versa. (3) The delivery tube should be removed from the water before the generator is allowed to cool — and again, why?

Thus can oxygen be made and collected for laboratory uses, and the number of bottles of it that can be made from one loading of the generator is limited only by the quantity of potassium chlorate present:

$$\text{Potassium chlorate} \longrightarrow \text{Oxygen} + \text{Potassium chloride}$$

PROPERTIES OF OXYGEN

In the foregoing discussion, references have been made here and there to such properties of oxygen as were pertinent to the phenomena under discussion at the time. But we have not yet undertaken a systematic investigation of oxygen as a "personality": how it is in *physical ways*, what it will and will not do in *chemical ways.*

Its physical properties and their importance. It is not necessary to go into the laboratory to make and collect oxygen in bottles in order to ascertain that it is *colorless*, *odorless*, *tasteless*, and *gaseous* inasmuch as these items are already known from the oxygen which comprises one-fifth of air mixture, hence is all around us. It is also obvious that oxygen must be *slightly soluble in water* since fish and aquatic plants must have it for their respiration needs. For other physical properties, such as the very low temperatures at which liquid and solid oxygen are possible, the extent of its solubility, and its density, pure oxygen must be obtained. Conse-

quently, these properties can be determined only in the laboratory through quantitative procedures performed with the most careful and painstaking technic. These findings have been obtained; and, while exact figures will have little specific use in this study, they are given below not only for such students as may be interested, but also to point to the fact that, from among the physical properties of oxygen, there are some which serve as evidence that oxygen is, in fact, an individual substance quite different from all other substances. And so, in summary manner, the physical properties of oxygen that have been stressed are:

Oxygen is colorless odorless tasteless gas, at ordinary temperatures slightly soluble in water.	These properties are characteristic of other gaseous substances as well as of oxygen, hence they do not serve to identify this substance.

Quantitative findings,

Extent of solubility, .049 vol. of oxygen in 1 vol. of water at 0° C. and standard pressure (p. 4.) Its boiling-point is − 182.5° C. freezing-point is − 218° C. density, 1 cc. at 0° C. and standard pressure weighs .001429 gm.	These properties are possessed exclusively by oxygen, hence identify it as a distinctive substance.

Importance. Do these physical properties have any important bearing in the concerns of man? Perhaps the fact that oxygen is colorless, odorless, and tasteless has no real vital significance, but from an *aesthetic* point of view these neutral properties of oxygen, as well as of other atmospheric substances, would seem to be a wise provision of nature. But the fact that oxygen is *gaseous* is of *vital* concern, since all land animals must have it in the gaseous state for their respiration needs. Furthermore, its very low boiling and freezing temperatures render it impossible for oxygen either to rain out or snow out of the atmosphere even at the very low temperatures in arctic regions or upper atmosphere. As a result, a continuous supply of gaseous oxygen is assured, thereby making it possible for land animals to live anywhere upon the earth, and for man to carry his explorations where he will. The *slight solubility* of oxygen in water also has its vital and important aspects. This vital importance as to aquatic animals has already been mentioned (p. 70); and for land animals oxygen must be carried in water solution from the lung cells into the blood

Chemical properties of oxygen and some consequences. The chemical properties of oxygen must be reckoned with continually.

Reacting as it does with so many substances, and being so omnipresent and all impregnating as it is, it is constantly engaging in reactions, not only in ways that are vital and important, but also in ways that are undesirable. Already miscellaneous bits of information have been presented here and there as to how oxygen behaves in chemical ways, but a more systematic study is now advisable. Therefore, let us proceed first to the study of its reactions *with other simple substances,* then to the study of its reactions *with compounds.*

Oxygen in reaction with simple substances. As a matter of fact, oxygen is the most cosmopolitan of all simple substances in its combining interests. Most simple substances will react with only a few other simple substances, whereas oxygen reacts with most of them with greater or less degrees of eagerness. For example:

Even at ordinary temperatures, fairly rapid reaction is possible between OXYGEN and	Only slow or inappreciable reaction at ordinary temperatures, but rapid reaction at elevated temperatures, can be expected from contacts between OXYGEN and	Only slow reaction, even at very high temperatures, can be commonly expected from contacts between OXYGEN and
Potassium	Magnesium	Aluminium
Sodium	Sulfur	Iron
Calcium	Carbon	Nickel
Phosphorus	Hydrogen	Tin
	and a number of other simple substances.	Copper
		Nitrogen
		and some other simple substances.

Oxygen does *not* react at all, even at very high temperatures, with

Silver
Platinum
Gold
Chlorine
Bromine
Iodine
Helium

Explanation for this varied behavior of oxygen. But why, asks the curious-minded student, does oxygen react more readily with some simple substances than with others and not at all with still others? And the answer is that *this difference lies in the differing tendencies of oxygen element, provided within oxygen substance, and the elements provided within other simple substances, to get together to make the compounds concerned.* Thus:

Between the substances, Oxygen and Phosphorus Oxygen and Potassium	Reactions take place speedily because of the marked tendency of oxygen element (provided in oxygen substance) and phosphorus and potassium elements (provided in phosphorus and potassium substances) to make the oxides concerned.
Between the substances, Oxygen and Magnesium Oxygen and Iron Oxygen and Nickel Oxygen and Copper	Reactions take place with respectively decreasing speeds because of the decreasing tendencies of oxygen element, and magnesium, iron, nickel, and copper elements (provided in magnesium, iron, nickel, and copper substances) to enter into combination to make the oxides.
Between the substances, Oxygen and Silver Oxygen and Platinum Oxygen and Helium	Reactions do *not* take place at all because oxygen and silver elements, oxygen and platinum elements, oxygen and helium elements are either very reluctant or else absolutely refuse to get together to make the oxides concerned.

The *matter products of such reactions* must be compounds since they are made by the direct combination of only two substances (p. 15), and they must be oxides since only two elements are respectively provided within the two simple substances, with oxygen as one of them. Word equations for two such reactions are as follows:

Oxygen + Potassium → Potassium oxide
Oxygen + Copper → Copper oxide

Chemical behavior of oxygen with compounds. The same reasoning applies as to what compounds oxygen *will* and *will not* react with as applies to reaction possibilities between oxygen and simple substances. Accordingly: *oxygen, the substance, can be expected to react with such compounds as contain elements that are interested in entering into combination with oxygen, the element.* For example:

Between the substances, Oxygen and Methane Oxygen and Ethylene Oxygen and Acetylene Oxygen and Carbon bisulfide	Compounds composed[1] of the elements hydrogen and carbon	Reactions are possible because the elements carbon and hydrogen in methane and ethylene, and the elements carbon and sulfur in carbon bisulfide are interested in combining with oxygen element provided in oxygen substance.

Oxygen + Methane → Carbon dioxide + Water
Oxygen + Carbon bisulfide → Carbon dioxide + Sulfur dioxide

[1] The class name that is applied to compounds that contain only the two elements hydrogen and carbon is *hydrocarbons*. There are hundreds of these compounds.

Between the substances, Oxygen and Carbon monoxide Oxygen and any Carbohydrate Oxygen and any Fat Oxygen and any Alcohol	Compounds composed of the elements carbon, hydrogen, and *some* oxygen (Carbohydrate, Fat, Alcohol)	Reactions are possible because the oxygen-liking elements (carbon in carbon monoxide, carbon and hydrogen in carbohydrate, fat, and alcohol), although already in combination with some oxygen, are not completely satisfied with it, hence they are able to combine with more of this element that is provided within oxygen substance.

Oxygen + Carbon monoxide → Carbon dioxide
Oxygen + Carbohydrate → Carbon dioxide + Water

On the other hand, oxygen substance cannot be expected to react (1) with compounds within which any oxygen-liking elements are already in combination with sufficient of this element; (2) with compounds that are composed of elements which are just as interested (or even more interested) in remaining in combination with each other within said compounds as in entering into combination with oxygen element. Thus:

The substances, Oxygen and Water Oxygen and Carbon dioxide Oxygen and Calcium carbonate	Do not react with each other because hydrogen within water, carbon within carbon dioxide, and calcium and carbon in calcium carbonate are already in combination with sufficient oxygen within these compounds.
The substances, Oxygen and Silver bromide Oxygen and Gold chloride	Do not engage in reaction because the elements silver and bromine within the compound silver bromide and the elements gold and chlorine within gold chloride have a greater liking for remaining in combination with each other than for entering into combination with the element oxygen.

Some practical consequences of these varied reactions with oxygen. Since oxygen is always present in earth's atmosphere no substances, simple or compound, which react with it *readily at ordinary temperatures* can be put to practical, everyday uses. Consequently, substances such as sodium and phosphorus are not met with commonly, but only in laboratories or in manufacturing concerns where they are handled carefully and stored with all necessary precautions.

Indeed, substances that can be put to use in the everyday concerns of most people, likewise substances that are safe just to have around, useful or not, must obviously be either such as react appreciably with oxygen only at elevated temperatures or not at all. Accordingly:

Carbon, component of coal; *celluloses,* components of wood and paper; *hydrocarbons,* components of gasoline, kerosene and fuel oils, can be safely stored if kept at ordinary temperatures, but, when so desired, they can be induced to react with oxygen for the purpose of making heat when raised to higher-than-ordinary temperatures that are easily obtained.

Aluminium, iron, nickel, and *copper* are useful for making cooking utensils and any other containers that are destined to meet with high temperatures because, among other reasons, although continuously in contact with oxygen, reactions between these metals and oxygen are exceedingly slow. *Platinum* would, of course, be the metal par excellence for such purposes, as well as for all purposes for which metals are used: physically, it is attractive, it is malleable and ductile as are other metal substances, and it has a very high melting-point; chemically, it does not react at all with oxygen even at the highest temperatures known; in fact, it reacts with very few other substances, but the known supply of this would-be useful substance is very limited.

Finally, and most fortunately, of the thousands of substances that are around us continually — in nature, in our homes and elsewhere — most are of the will-not-react-at-all-with-oxygen variety. As a matter of fact, the phrase "burned to the ground" is an expression of real significance in that once a conflagration has reached the "ground" that must be the end of it since "ground": namely, the solid crust of the earth where most of earth's substances are located, is a mixture for the most part of substances — clay, feldspar, and calcium carbonate among them (p. 41) — which cannot possibly react with oxygen.

Varieties of products from reactions with oxygen. *A matter product.* As is true of *all* reactions, a matter product must result from every reaction with oxygen: namely, the substance or substances which are made. And, as already noted, these substances are made from elements provided previously within the beginning substances (pp. 14, 18, 21.)

An energy product. But from every reaction that includes *oxygen* as one of the beginning substances, along with the matter product an energy product must also be made. It is common knowledge that *heat,* which is one variety of energy, is made during many such reactions. For example: when oxygen reacts with carbon during any burning, or with celluloses, or with fats, or with the hydrocarbons (p. 77) of gasoline, *heat* is a product:

Matter products	*Energy product*
Oxygen + Carbon ⟶ Carbon dioxide	Heat
Oxygen + Fat ⟶ Carbon dioxide + Water	Heat
Oxygen + Hydrocarbons ⟶ Carbon dioxide + Water	Heat

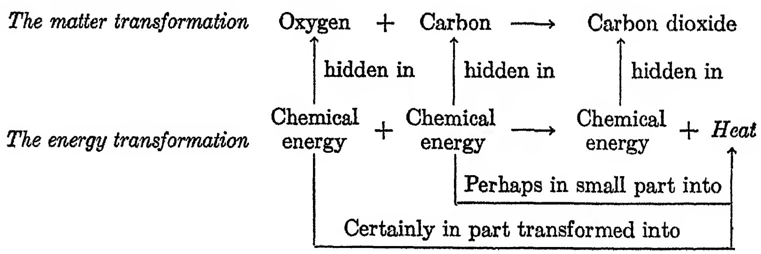
But other varieties of energy can also be made. Thus: when oxygen reacts with the hydrocarbons of gasoline in the cylinders of an automobile, *kinetic energy*, the energy responsible for motion of matter, is made. Of more vital concern is the fact that within muscle cells, when oxygen reacts with glucose or with fats, as the matter products carbon dioxide and water are made, so also, and at the same time, *kinetic energy* is made for the motion of body parts:

In cylinders of automobiles *Matter products*	*Energy product*
Oxygen + Hydrocarbons (in gasoline) ⟶ Carbon dioxide + Water	Kinetic energy
In muscle cells	
Oxygen + Glucose ⟶ Carbon dioxide + Water	Kinetic energy

Source of the energy product. As for the source of the energy product from any reaction involving oxygen, *during the reaction it is made mostly from a portion of a variety of energy, called chemical energy, which is hidden within the substance oxygen;* [2] *perhaps, also, to a slight extent, from a portion of this hidden energy, or chemical energy, within the partner substance.*

Related matter and energy transformations. Thus it is that, during reactions involving oxygen, two related but quite different transformations occur: a matter transformation during which new substances are made, and an energy transformation during which an energy product is made. Let this be made clearer in the light of the following examples:

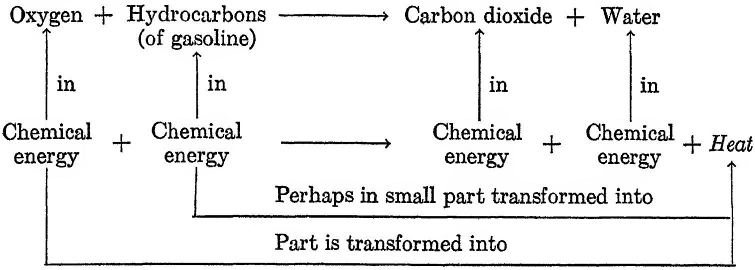
1. When coal burns,



[2] A. P. Mathews, *Principles of Biochemistry*, Wm. Wood and Company, 1936, p. 491.

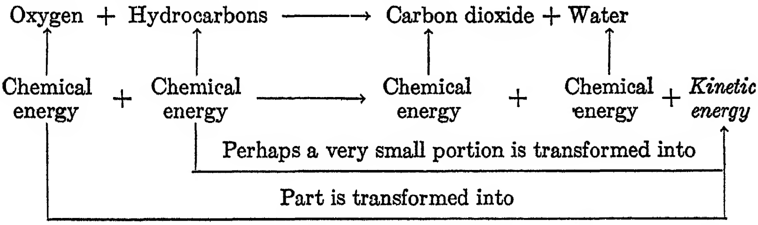
Interpreted: When oxygen reacts with carbon to make carbon dioxide, part of the chemical energy in the keeping of the oxygen (and perhaps a very small part of that which is in the keeping of the carbon) is transformed into a *heat product;* the rest of these hidden or chemical energies remain the same variety of energy within the resulting carbon dioxide.

2. When gasoline reacts with oxygen in the kitchen stove,



Interpreted. When oxygen reacts with hydrocarbons in a "gasoline burner" to make the *matter products* carbon dioxide and water, part of the chemical energy in the keeping of oxygen (perhaps a very small part of that within the hydrocarbons) is transformed into *heat* which constitutes the *energy product* of this reaction; the rest of said chemical energy remains this energy but distributed within the carbon dioxide and water.

3. However, when this same reaction takes place within the cylinders of gasoline-run machinery, while the matter products are the same, a different energy product, namely kinetic energy, results:



This fact, that both matter and energy products result from reactions in which oxygen is one of the beginning substances, is of vast importance in living concerns and it will be the subject of our next study. The fact that energy transformations, with or without oxygen as one reacting party, constitute one aspect of many chemical changes will be dealt with more extensively a little later. (Chapter VIII.)

FUNCTIONING OF OXYGEN

Our final study in respect to oxygen substance is in reference to its functioning in the affairs of man: first, man's living, hence vital, need for it; second, the functions of oxygen in man's external

concerns. Doubtless all informed people these days know that, for some reason or other, oxygen is essential in such ways, but very few people know why. Our aim will be to take at least one forward step in finding an answer to these "whys"; already a start has been made in this direction in the foregoing study.

Oxygen is essential for living. The living body is one which is able to make within itself the *kinetic energy* that is essential for the motion of its body parts: for continual beating of the heart, for muscular control of respiratory movements, and for all other muscular contractions. The living body is also able to make its own *heat* for keeping itself warm and *any other energies* that may be required. When the body has lost the ability to make these energies within itself, it is no longer a living or "quick" body, but a dead one; it is no longer a warm body, but a cold one.

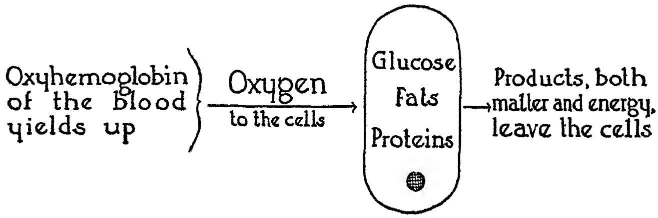


Fig. 19

There arises, then, the significant question as to the source from which the living body obtains these energies. And this brings us directly to the all-important subject of the vital need for oxygen, since, for the most part, these energies are made mostly from part of the chemical energy within the substance oxygen, this substance being carried by the hemoglobin from the lungs to the cells for such purpose (Fig. 19).

While glucose, fats, and proteins are the initial substances concerned, the actual reacting partners for oxygen are probably metabolic intermediate substances obtained from these sources.

Thus when the cells concerned are called upon to make any variety of energy for their living needs, they requisition oxygen brought to them by the blood and cause it to react with glucose (usually), or with some fat or protein at hand (Fig. 19); and, as the matter products of these reactions are made, part of the hidden or chemical energy in the keeping of the oxygen is transformed into the desired kinetic energy or such other energy as may be

in demand at the time. Word equations for these related matter and energy transformations are as follows:

$$\begin{array}{ccccccccc} \text{Oxygen} & + & \text{Glucose} & \longrightarrow & \text{Carbon dioxide} & + & \text{Water} & & \\ \uparrow & & \uparrow & & \uparrow & & \uparrow & & \\ \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & \longrightarrow & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\textit{Kinetic energy}\\ \text{or any other}\\ \text{variety of}\\ \text{energy needed}\end{array} \end{array}$$

Interpreted: As oxygen reacts with glucose within the cells to make carbon dioxide and water, part of the chemical energy of the oxygen (perhaps a very small part of the chemical energy of glucose) is transformed into kinetic energy or such other energy as is required at the moment. The rest of the chemical energy remains chemical energy in the matter products carbon dioxide and water.

$$\begin{array}{ccccccccc} \text{Oxygen} & + & \text{Fats} & \longrightarrow & \text{Carbon dioxide} & + & \text{Water} & & \\ \uparrow & & \uparrow & & \uparrow & & \uparrow & & \\ \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & \longrightarrow & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\textit{Kinetic energy}\\ \text{or another}\\ \text{variety of}\\ \text{energy}\end{array} \end{array}$$

$$\begin{array}{ccccccccccc} \text{Oxygen} & + & \text{Proteins} & \rightarrow & \text{Carbon dioxide} & + & \text{Water} & + & \text{Urea} & & \\ \uparrow & & \uparrow & & \uparrow & & \uparrow & & \uparrow & & \\ \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & \rightarrow & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\textit{Kinetic}\\ \textit{energy}\\ \text{or some}\\ \text{other}\\ \text{variety}\\ \text{of energy}\end{array} \end{array}$$

What happens to the products. The matter products from these several reactions, as signified by the foregoing word equations, are water, carbon dioxide, and urea. The *carbon dioxide*, probably in part within the cells themselves and in part within the lymph and blood, reacts with water and other substances to make carbonic acid and sodium bicarbonate. But at lung cells the latter substance is remade into carbonic acid which, in turn, decomposes to remake water and carbon dioxide. The latter diffuses through lung membranes and is exhaled. Essentially, therefore, the carbon dioxide made in the cells is eventually, for the most part, exhaled as carbon dioxide from the lungs (Fig. 20), the carbonic acid and sodium bicarbonate being intermediate but useful substances.

The *urea* enters the lymph bathing the cells, then the blood. Most of it is removed from the blood by the kidneys and excreted in the urine; some, however, is excreted by the sweat glands of the skin (Fig. 20).

Water follows the fate of all water that contributes to the blood stream. Considerable is excreted through the lung membranes and exhaled, hence the moisture of the breath; some is excreted through the kidneys into the urine; considerable is excreted through the skin cells (Fig. 20).

The energy products. Kinetic energy made within muscle cells, having performed its mission for moving body parts, is transformed into heat (Fig. 20), which on its way to the outside of the body keeps the cells, lymph, blood, and all body parts warm. At the surface layers, lung and skin, a considerable

portion of this heat serves to transform water from liquid to the gaseous state, becoming thereby latent heat of vaporization within the exhaled water vapor (574 calories for every gram of water at 40° C. changed to water vapor, likewise

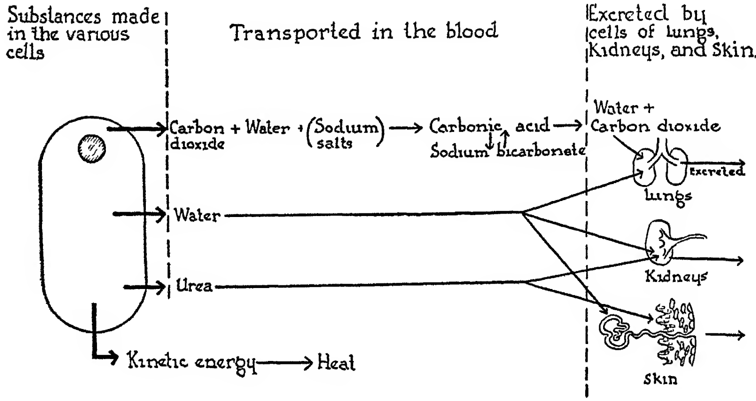


FIG. 20

at 40° C.). But some of this heat is radiated still as heat; hence the familiar phenomenon of the warming of a room by living people or the warming of a bed in which a person is covered by heat-insulating blankets.

Other important functionings of oxygen. In the external concerns of man *oxygen functions* (1) *as a party in providing much of the world's heat* for keeping buildings warm, for cooking foods, as well as for other purposes; and (2) as *a party for providing kinetic energy* for moving the world's machinery. And again, oxygen is able to function in these ways because it holds within its keeping hidden or chemical energy, part of which — when oxygen engages in reactions with selected substances — becomes available for transformation into these desired energies. Studies in this connection have already been made (pp. 76–77) and will receive attention again in a later chapter (pp. 97–98).

Toward quite a different end, *oxygen functions* in our external affairs as (3) *a party to getting rid of the proteins* of dead plants and animals. This is accomplished in the process commonly called decay and involves a whole series of reactions in many of which bacteria play an active part by providing enzymes for speeding up said reactions to appreciable proportions. But with only the beginning and end substances mentioned, the following word equation tells of these reactions inclusively and briefly:

$$\text{Proteins} + \text{Oxygen} \longrightarrow \text{Nitrogen} + \text{Carbon dioxide} + \text{Water}$$

An energy product, namely heat, is made during these reactions along with the matter products, but not being of chief importance in this instance, it is not stressed.

Benefits that result from these reactions are: (1) objectionable proteins of dead plants and animals are thereby removed by nature; (2) a supply of nitrogen is thus assured for the purpose of engaging in reactions whereby proteins are remade for more living plants and animals; and (3) this supply of inert nitrogen at the same time dilutes the ever present, ever needful, but more active oxygen.

The supply of oxygen for these uses. For everyday uses, the dilute oxygen of earth's atmosphere is entirely adequate — a fact for which we should be devoutly thankful. For the purpose of making heat we must buy the partner substances for oxygen — carbon of coal, celluloses of wood, hydrocarbons of gasoline or illuminating gas. For the making of energies for living needs we must buy such starches, proteins, and fats as will eventually — through digestive and assimilative processes — provide reacting partner substances for oxygen within the cells. But oxygen itself, the substance which actually provides most of the available energy for transformation into heat and other energies outside the body and into desired energies within the cells, we can have for the taking and without cost.

Maintenance of this oxygen supply. Since oxygen is being continuously removed from the atmosphere for respiration needs of the world's animals as well as for various burnings, the question arises as to how this essential substance gets put back into the atmosphere. And this brings us again to that reaction which takes place during the daytime in chlorophyll cells of plants whereby they make not only carbohydrates for their own needs but *oxygen* which they discard (pp. 66, 101). Thus, in this as in other ways, plants become essential handmaidens to the needs of animals.

Commercial supplies of oxygen and their uses. Commercial supplies of oxygen are packed into large tubes for large uses and into small tubes for small uses (Fig. 21). *Therapeutically,* this highly concentrated oxygen is used to contribute to living needs for such purposes as bringing about rapid recovery from anesthesia, for reviving those suffering from asphyxia, and for the relief of anoxemia in conditions, similar to those produced by pneumonia, when lung areas available for oxygen absorption are less than normal due to congestion.

Toward *exploration* and *industrial* ends, commercial supplies of almost pure oxygen are used for living needs when man carries his activities either where there is no oxygen or where its concentration is very low. So it is that deep-sea diving, underwater explorations and constructions, and salvaging of sunken vessels have become possible only since commercial supplies of oxygen have been made available for feeding down to the workmen concerned. Stratosphere flights, and the making of high altitudes in open planes, and long-distance high-altitude flights, such as those over Mount Everest, have been rendered possible only through the availability of highly concentrated oxygen for men to take along with them to contribute to their vital needs when engaged in such ventures.

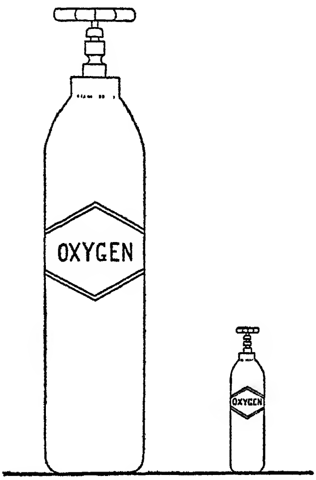


FIG. 21. Commercial Supplies of Oxygen

In the *construction* of our modern subterranean and under-water traffic tunnels, which necessitates the carrying forward of excavations in a series of sealed chambers, oxygen must be fed in to the workers; without this possibility such pieces of engineering would be out of the question.

And commercial supplies of almost pure oxygen, besides meeting the living needs of workmen, have played still another part in rendering the foregoing activities possible. The building of the aeroplanes themselves, of the stratosphere gondolas, and of the underwater tubes have called for weldings of their metal parts; and these weldings have become possible only since the *high temperatures* necessary for the softening of the metals (p. 28) concerned have been obtainable through the more rapid burning of almost pure oxygen with acetylene or with hydrogen.

Indeed, many other progressive leaps from the "then," of not so many years ago, to the "now" of modern times have been due, in great part, to the availability of these high temperatures for metal weldings and construction and the consequent needs for metal repairings. Hereby have been rendered possible: the passing of horse-drawn wooden plows and man-wielded scythes, and the incoming of tractors, binders, and combines, thus revolutionizing

farming procedures; the passing of wood-constructed wagons, carriages, railway coaches, and ships to be replaced by trucks, automobiles, all-steel coaches, and ocean liners; the passing of wooden bridges, replaced by safer and more graceful metal spans of today; the passing of two- or three-story buildings, and the incoming of iron framework for taller and taller structures.

Questions

1. Make summary statements as to the chemical behavior of oxygen (a) with other simple substances, (b) with compounds. Illustrate by reference to specific examples.

2. What, if any, reaction would you expect to take place upon heating to a sufficiently high temperature each of the following in contact with oxygen: carbon, platinum, tin, clay, cellulose, carbon dioxide, hydrogen sulfide? Account for difference in tendency of these substances to react with oxygen. If a reaction is to be expected, assemble the word equation for the same.

3. a. What matter products can be expected from reactions between oxygen and sulfur? Oxygen and any hydrocarbon?
   b. Give word equations for related matter and energy transformations that are involved in these reactions.

4. Give two reasons why it is advisable for each student to have an asbestos mat readily at hand for use in the chemistry laboratory.

5. Interpret the word equations given on page 79 for the related matter and energy transformations that take place when: (a) oxygen reacts with a fat; (b) oxygen reacts with a protein.

6. Acetylene is a hydrocarbon, meaning that it is composed of the two elements hydrogen and carbon. Why is it able to react with oxygen? Give word equation for this reaction — the matter transformation only.

7. Name four factors that affect the speed of chemical reactions with oxygen, telling how each functions. Illustrate by reference to specific examples.

8. a. Why do fluffed-up paper and oxygen burn more rapidly than a log of wood and oxygen?
   b. Why is helium, although more dense than hydrogen, preferred for inflating dirigibles or any passenger-carrying balloons?

9. List several common processes whereby the oxygen supply of the atmosphere is being constantly drawn upon for reactions. How is the oxygen content of earth's atmosphere maintained? Why is it important that atmospheric oxygen is diluted with nitrogen?

10. Why is oxygen essential for living and why can it function in this respect? Where does this vitally important functioning take place? What reacting partner substances are provided? What reactions take place? What is the source of the desired energies? What happens to the energy products? To the matter products?

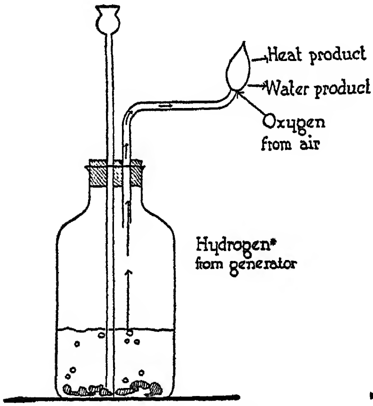
11. For what therapeutic uses have commercial supplies of oxygen proved to be of value?

12. What are some of the most important uses for commercial supplies of oxygen? Cite a few of the developments of modern civilization which have become possible only through the agency of commercial supplies of oxygen.

CHAPTER VII

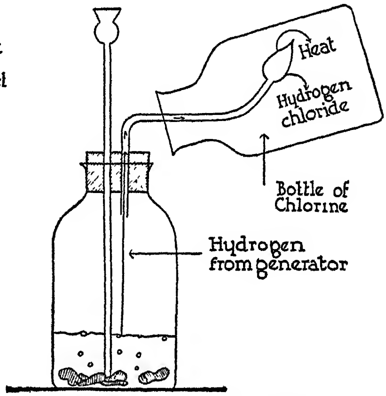
Burning or Combustion

The word *burning,* likewise its synonym *combustion,* is commonly used in reference to several phenomena which have no relationship from a chemical viewpoint. Therefore, for the sake of a common ground of understanding, it becomes necessary to select one of the several meanings for these synonymous words and to use them consistently from now on only in respect to the specific



Hydrogen + Oxygen → Water
↓ ↓ ↓
Chemical energy + Chemical energy → Chemical energy + Heat and Light

FIG. 22. Burning of Hydrogen and Oxygen



Hydrogen + Chlorine → Hydrogen chloride
↓ ↓ ↓
Chemical energy + Chemical energy → Chemical energy + Heat and Light

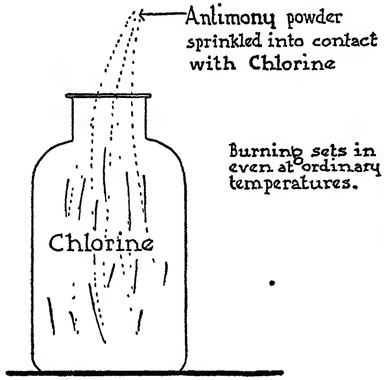
FIG. 23. Burning of Hydrogen and Chlorine

* *Great caution* is necessary in the burning of hydrogen with oxygen (p. 98).
** Hydrogen is made from reaction between zinc and hydrochloric acid (dilute). All air must be completely displaced from the generator before the emerging jet of hydrogen is lighted.

phenomenon defined. So, by *burning* or *combustion will be meant any chemical reaction between two substances which produces heat as an energy product, and which is proceeding so rapidly that the heat becomes apparent and is accompanied by a light product.*

For example: when any of the pairs of substances specified in the accompanying diagrams (Figs. 22 to 25) are brought in contact with each other, and a sufficiently high temperature level obtained, a burning reaction will set in.

A study of this selection of examples of burning possibilities should dispel any notion which the student may have that oxygen must always be one of the participating substances in the burning phenomenon. At the same time, it is not surprising that people should commonly arrive at this incorrect notion, since it is a fact

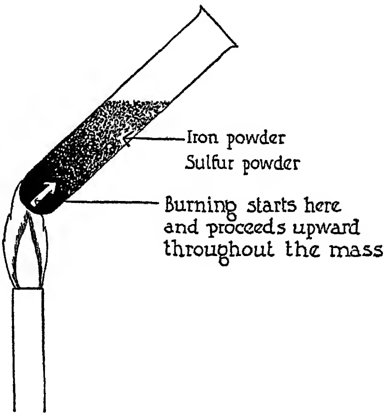


Antimony + Chlorine → Antimony chloride

↓ ↓ ↓

Chemical energy + Chemical energy → Chemical energy + Heat and Light

FIG. 24. Burning of Antimony and Chlorine



Sulfur + Iron → Iron sulfide

↓ ↓ ↓

Chemical energy + Chemical energy → Chemical energy + Heat and Light

FIG. 25. Burning of Iron and Sulfur

that those burnings which the great majority of people personally experience do require *oxygen* from the air mixture as one of the substances concerned. And since burnings with oxygen are of especial importance in the concerns of man, the discussion of this phenomenon from now on will be in direct reference to such contacts.

BURNING WITH OXYGEN AS ONE REACTING PARTY

Requirements. For burning with oxygen the following essentials must be obtained:

1. A partner substance that is capable of reacting rapidly with oxygen.
2. Contact between oxygen and the partner substance.
3. The temperature level at which the reaction can take place with burning speed, usually called *kindling temperature.*

Partner substances. Among partner substances that are commonly encountered by all people, or by students in the laboratory,

which are capable of reacting with oxygen at burning speed are the following:

In everyday concerns

Carbon (component of coal, coke, charcoal)
Celluloses (component of wood, paper)
Hydrogen, Gaseous hydrocarbons[1], Carbon monoxide — components of illuminating gas
Liquid hydrocarbons[1] (components of gasoline, kerosene, fuel oils)
Solid hydrocarbons[1] (components of paraffines)
Grain alcohol, Wood alcohol, Fats — (p. 74)

In the laboratory

Potassium
Sodium
Calcium
Magnesium
Phosphorus
Sulfur
Hydrogen
Methane, Ethylene, Acetylene — hydrocarbon components of illuminating gas
Ether
Carbon bisulfide

Contact between oxygen and the partner substance. This condition is so obviously essential that no discussion is necessary. But it is interesting to note that — of those substances listed above which are capable of burning with oxygen — carbon, celluloses, paraffines, and fats are commonly always in contact with oxygen, so that all that is necessary for their respective burnings is kindling temperature. The other burnable substances listed should, of course, be stored in such a way as to keep them out of continuous contact with oxygen.

Kindling temperature. *Varies with tendency of substances to react.* One factor which determines the temperature level at which reaction with burning speed will set in is the tendency of the substance to react with oxygen. For example:

Given pieces of phosphorus, of calcium, and of carbon of identical areas of contact with dilute oxygen of the atmosphere, the kindling temperature of phosphorus and oxygen will be slightly above ordinary, of calcium and oxygen will be higher, and of carbon and oxygen will be considerably higher.

Varies with surface of contact. But the more important factor in determining kindling temperature is the surface of contact between oxygen and its partner substance. Let this fact be made more convincing through the following well-known instances:

1. Cellulose of the *same wood* and oxygen can have a whole range of kindling temperatures:

If compact, as in a log of wood, in contact with dilute oxygen . . . . kindling temperature is high.
If in kindlings, piled loosely in contact with dilute oxygen . . . . kindling temperature is lower.
If in loose shavings in contact with dilute oxygen . . . . kindling temperature is still lower.

[1] See footnote, p. 73.

2. Oxygen with partner substances which are gaseous or volatile liquids have *low* kindling temperatures because of their ability to get automatically into large areas of contact. Furthermore, the greater the volatility of the liquid substance the lower will be the kindling temperature concerned. Thus:

Kerosene with dilute oxygen............a low kindling temperature.
Gasoline with dilute oxygen............a lower kindling temperature.
Ether with dilute oxygen...............a very low kindling temperature.
Illuminating gas mixture with dilute oxygen............................a very low kindling temperature.

In fact, all the foregoing low kindling temperatures are so far down in the temperature scale that they are obtainable by such means as the burning match, the lighted cigarette stub, or the "live coal" from the fire. Moreover, kindling temperatures become increasingly lower in increasingly higher concentrations of oxygen; as a consequence they are lower in oxygen tents than in dilute oxygen of normal air, hence burning hazards in the former become correspondingly greater.

Control of burning. By control of burning is meant here, control of speed of burning, putting out fires, and fire prevention, all of which call for a manipulation of the three requirements for burning.

Control of speed of burning involves control of surface of contact between oxygen and the partner substance: the greater the surface of contact the greater being the speed of burning and vice versa, a rule which is so familiar in everyday practice in fire control that the student should be able to supply examples in plenty.

Putting out fires necessitates one of two procedures: either cutting out contact between oxygen and the partner substance, or lowering the temperature of the burning masses below the kindling temperature of the reacting parties.

Accordingly, a woolen blanket, or a coat or rug, or a sheet of asbestos, or a shovelful of sand thrown over the burning masses, or a stream of nonburnable gas directed over the same are all effective in putting out fires, in that layers of either difficultly burnable or nonburnable substances are thus injected between oxygen and the burning partner substances. On the other hand, a continuous play of a stream of water will eventually serve to lower the temperature of the substances concerned below their kindling temperature; the same end may be accomplished by the chill produced by suddenly expanding gases released from a fire extinguisher.

Fire prevention. Unfortunately, many people do not make it a habit of their lives to give careful, conscious thought to fire pre-

vention when fires are not desired; if they did nine-tenths or more of undesired fires would not take place. There are just *three* specified requirements for burning with oxygen; given all three and burning will set in whether desired or not, but *if only one of these requirements is absent there can be no burning.*

In the everyday concerns of all people the first two requirements are always provided here or there: wood shavings, or excelsior, or fluffy waste paper in contact with oxygen; flimsy cotton draperies or clothing in contact with oxygen; dry leaves or grass in like contact. And kindling temperatures in these instances are low, therefore they must be carefully avoided.

The first two requirements for burning are likewise obtained in an operating room whenever ether and oxygen are in contact, or more hazardous still whenever ethylene and oxygen are in contact. Consequently, once again, it is kindling temperature that must be guarded against; even the glow of the fading match or cigarette must not be there, and it is imperative that there be no defective electric switch or wiring. And the same sort of hazard attends the cleansing of gloves or garments with volatile and burnable liquid substances.

It would be possible to continue on and on in respect to other well-known burning hazards and equally well-known precautionary measures, excuses for the lack of observance of which — the "I didn't know," or "I wasn't thinking" — are simply *not acceptable* from supposedly responsible persons.

Spontaneous combustion. Spontaneous combustion is another loosely and vaguely used expression. Quite commonly, when people are baffled in attempts to find a "why" for an unexpected fire outbreak they shake their heads and say mysteriously "spontaneous combustion," with the implication that in this particular fire the laws of nature have been defied, which, undoubtedly, is just not the case. More likely than not, the offending kindling temperature has been carelessly or unwittingly provided by one or another of the above suggested means.

For the chemist, however, spontaneous combustion has a very specific significance, as follows. Sometimes oxygen and the partner substance "build up" to their kindling temperature through the accumulation of heat from their slow reaction or rusting, in which case, the instant said temperature level is thus obtained, burning springs into action. Burnings with kindling temperatures of such origin are properly called spontaneous combustion. Here are instances:

A fire breaks out suddenly in a closet in which the painter has left a bunch of cotton waste carrying linseed oil and carelessly forgets about it so that it lies there for days unnoticed. Now, as it happens, *linseed oil and oxygen* react slowly at ordinary temperatures, i.e., they rust:

$$\begin{array}{ccccccccc} \text{Linseed oil} & + & \text{Oxygen} & \longrightarrow & \text{Carbon dioxide} & + & \text{Water} & & \\ \downarrow & & \downarrow & & \downarrow & & \downarrow & & \\ \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & \longrightarrow & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \text{Heat} \end{array}$$

The *heat product* is made slowly; but since cotton waste is a poor conductor of heat, and since there is little air circulation in the closet to carry away the heat as made, it accumulates in the waste, the temperature of which mounts higher and higher until the linseed oil and oxygen attain their kindling temperature, and at that instant they begin to react at burning speed.

A fire starts spontaneously in a barn where the farmer has impatiently stowed away "uncured" hay. The barn doors are closed, the days pass, and this is what happens: some substances, perhaps proteins of uncured hay, or their decomposition products, carry on a slow reaction with oxygen, and this goes on for some time. Along with the matter products of the reaction *a heat product is made slowly.* But the hay is a poor heat conductor, also there is little air current to distribute the heat as made, hence it accumulates in the hay mow with the resulting mounting temperature. *If* this continues undisturbed until kindling temperature of oxygen and a reacting partner substance is obtained, then sure as fate, at that instant, burning will set in.

BURNING WITHOUT OXYGEN

Finally, before leaving this subject, the student should be reminded once again, that *oxygen is not necessarily always one of the substances participating in burning reactions.* As has been said previously, in such burnings as take place commonly in everyday concerns it is, to be sure, one of said substances, but in laboratories and other less usual situations, burnings not involving oxygen are possible (pp. 84–85).

Questions

1. After the concept defined in this chapter, what constitutes a burning reaction? Most people believe that oxygen is essential to all burning reactions; is this correct? Justify your answer.

2. What three conditions must be met in order that any burning may take place? What three conditions for burning *with oxygen* must be met?

3. Although loose papers burn readily, books are relatively difficult to burn; account for this difference. Kerosene and gasoline are both mixtures of liquid hydrocarbons: explain why gasoline constitutes a greater fire hazard than kerosene. Why is illuminating gas an even greater fire hazard?

4. When material is described as highly combustible, what should be meant? Illustrate. When a building is claimed to be of "fireproof" construction, what is meant? What conditions should be met (as far as possible) in the construction of such a building?

5. The concentration of oxygen within an oxygen tent is frequently maintained at about 50 per cent, as compared with 20 per cent in ordinary air.

a. What effect would this have on the kindling point of oxygen with burnable substances within the tent? What burnable substances are likely to be present at all times? Occasionally?

b. How would this affect the speed of burning should a fire accidentally occur, as compared with the speed of burning in common air? Why?

c. What precautions in particular should, therefore, be strictly observed by all persons in or about an oxygen tent?

6. Why is ethylene more hazardous, as to burning, than ether? Why the hazard as to cleaning gloves with gasoline?

7. Explain the function of bellows in speeding-up the burning of wood or coal?

8. Mention two effects, as to burning, that are produced by a large area of contact between the burnable substances.

9. What two conditions encountered within woods during a dry season are always favorable to the outbreak of forest fires? What one condition remains to be provided? By what several means is it frequently obtained?

10. How would you proceed to build a coal fire in a stove or fireplace? Give reasons.

11. When a fire outbreak is due to "spontaneous combustion" what may have occurred?

12. Suppose you encounter burning in a waste paper basket, what would you do to stop it? Consider two possible procedures and explain how each would function.

13. Make a list of substances and materials with which you come in frequent contact and which constitute potential fire hazards. Think over your habits in relation to these contacts and consider whether or not you are observing all necessary precautions for fire prevention.

CHAPTER VIII

Chemical Changes May Involve Energy Transformations

ENERGY

The fact that *an energy transformation may occur along with the matter transformation during the course of a chemical reaction* has been introduced in the preceding chapter. It is proposed now to carry this study further. But first it would be well to gather together some specific items concerning energy. With some of these items the student will be more or less familiar.

What is energy? No one knows what energy really is. People in general have limited acquaintance with some varieties of energy, such as heat and light, and have learned how to put them to use. Scientists have gathered an astounding mass of knowledge about all known varieties of energy. But what energy *is* belongs still among the great mysteries of nature.

Some varieties of energy. *Heat* is as familiar as any of the energy manifestations. People are equipped with sensory organs which render them aware of higher or lower temperature levels, hence of the presence of more or less heat collected by the matter involved: the air of the room, water, or other heat-collecting material. The phenomenon of *light* energy is familiar within limits. Humans are equipped to sense the presence of such light energy as is responsible for colors from red to violet, but they are blind to ultra-violet and infra-red light. *Kinetic energy,* or that energy which is responsible for the motion of matter, one can be made aware of in various ways: through the eyes due to the change of position of the moving mass, or through the ears because of the resulting swish of the air in the wake of the more or less rapidly moving object. On the other hand, humans are utterly blind to *electricity.* It can be transformed into heat which one can feel or into light which one can see, but then it has ceased to be electricity and one must reason one's way back to it as the precursor of the heat or the light. But, one may say: "I do certainly feel electricity when I put moist fingers on two electric terminals"; however, what one really feels is not electricity but the kinetic energy of quivering muscles that has been made from the electricity.

Measuring possibilities. Inasmuch as energy can be sensed only in association with matter, it follows that it can be measured only in terms of a definite measurable effect produced in respect to matter. Accordingly, adopted measuring units for heat, called the *small calorie*, *large calorie* and *British thermal unit*, *are in respect to temperature changes that the quantities of heat concerned produce with water as the collecting medium.* Thus:

One ***small calorie*** (cal.), or the *gram calorie*, of heat is the heat quantity which is sufficient to raise the temperature of 1 gram of water through 1° C.
One ***large calorie*** (Cal.), or the *kilogram calorie*, of heat is the quantity of heat which will raise the temperature of 1 kilogram of water through 1° C.
One ***British thermal unit*** (B.T.U.) of heat is the quantity of heat which will raise one pound of water through 1° F.

And as measuring rods for heat these units function as do other units in respect to other measurings. For example:

20 Calories would be enough heat to increase the temperature of

1 kilogram of water through 20° C.
5 kilograms of water through 4° C.
10 kilograms of water through 2° C.

There is more to the basis upon which a *unit for measuring kinetic energy* has been obtained than it is advisable to enter into in this study. Therefore we shall use a unit for measuring this energy, called a *foot-pound*,[1] that has been established in respect to a related energy phenomenon. For our purposes, then, *a foot-pound shall mean the quantity of kinetic energy that is required to lift one pound of matter through one foot of distance.* Which being true would mean that:

1. For climbing a flight of stairs 20 feet high a person weighing 120 pounds and one weighing 140 pounds must make, within the cells of the muscles concerned, the following respective quantities of kinetic energy:

$$120 \text{ (lb.)} \times 20 \text{ (ft.) or 2400 foot-pounds of kinetic energy,}$$
$$140 \text{ (lb.)} \times 20 \text{ (ft.) or 2800 foot-pounds of kinetic energy.}$$

2. For carrying an automobile and load weighing 2500 pounds up a hill 200 feet high from base to top, 2500 (lb.) $\times$ 200 (ft.) or 500,000 foot-pounds of kinetic energy must be made; this kinetic energy is made within the cylinders of the automobile, during the reactions concerned, from chemical energy provided mostly within the initial oxygen substance as one party to said reactions (pp. 77, 80).

[1] This really is a unit for measuring what the physicist calls *work*. The related kinetic energy unit is a foot-poundal, the basis for which involves considerations which it is not desirable to enter into in this study. But, since there is an exact relationship between this more involved foot-poundal kinetic energy unit and the foot-pound work unit (1 foot-pound = 32.174 foot-poundals), there is some justification for looking upon the more easily comprehended foot-pound as a kinetic energy unit equivalent.

As for *electricity*, it is made, distributed, and used on a *kilowatt-hour* measuring basis, and any thinking person can reason as follows:

1 kilowatt-hour of electricity must be 1000 times more than 1 watt-hour of electricity; 1 watt-hour must be 60 times more electricity than 1 watt-minute; 1 watt-minute of electricity must be 60 times more than 1 watt-second of this energy.

So far, so good, but to carry this reasoning as to these units still further must necessitate knowing what constitutes a watt-second of electricity. This, of course, is known to students of electricity, but for our purposes suffice it to say: *first* that a *watt-second of electricity* and the correspondingly larger *kilowatt-hour of electricity* are based upon very definite, measurable effects produced by this energy in respect to matter; and *second* that these units constitute very definite quantities of electricity which serve as small and large units respectively for measuring this variety of energy.

Energy transformations. ***Various possibilities.*** That some varieties of energy are easily transformed into other energies is a well-known fact. The possibility of the transformation of

$$\text{Kinetic energy} \xrightarrow{\text{into}} \text{Heat}$$

is exemplified in the familiar making of heat from the kinetic energy of the moving parts of machinery against each other. And of *vital importance* is the transformation of the kinetic energy, made within muscle cells for the motion of body parts, into the heat which keeps the body warm (pp. 78–79). Also of importance are the transformations of:

$$\text{Kinetic energy} \xrightarrow{\text{into}} \text{Electricity}$$
$$\text{Electricity} \xrightarrow{\text{into}} \text{Kinetic energy}$$
$$\text{Electricity} \xrightarrow{\text{into}} \text{Heat}$$
$$\text{Electricity} \xrightarrow{\text{into}} \text{Light}$$

Most *electricity* of commerce is *made from the kinetic energy* of waterfalls or of expanding steam. And, in turn, large quantities of this *electricity* are distributed here and there for *retransformation into kinetic energy* for such purposes as the running of trolley cars and trains; also immense quantities are conducted into homes, stores, manufacturing plants, and other places for *transformation*, as desired, *into heat* or *into light*, or *into kinetic energy*.

Energy transformations are quantitative. A definite number of foot-pounds of kinetic energy makes a definite number of kilowatt-

hours of electricity, or a definite number of Calories of heat, and vice versa. But in order that this fact may be made more convincing, here are actual quantitative transformation values that have been discovered as the result of numerous very careful and painstaking laboratory measurings:

3087 foot-pounds of kinetic energy $\xrightarrow{\text{make}}$ .0011 kilowatt-hour of electricity $\xrightarrow{\text{makes}}$ 1 Calorie of heat

.0011 kilowatt-hour of electricity $\xrightarrow{\text{makes}}$ 3087 foot-pounds of kinetic energy

Hence, 3087 foot-pounds of kinetic energy $\rightleftarrows$ 1 Calorie (large) of heat

Herein lies the reason why the making of electricity can be placed on a very definite quantitative basis: why the manufacturer can figure exactly as to how much electricity he can make from this or that quantity of kinetic energy; likewise why he can determine with great exactness how much heat, or light, or kinetic energy the consumer can depend upon obtaining from every kilowatt-hour of electricity. Thus can the manufacturer afford to make electricity, and the consumer afford to buy this energy.

Moreover, since energy transformations are quantitatively exact, it follows that it should be possible to measure any one variety of energy in terms of units established primarily for measuring other energies. So it is that:

3087 foot-pounds of heat is 1 Calorie of heat.
3087 foot-pounds of electricity is .0011 kilowatt-hours of electricity.
1 Calorie of electricity is .0011 kilowatt-hours of electricity.
1 Calorie of kinetic energy is 3087 foot-pounds of kinetic energy.

And, indeed, nutritionists usually do just this, meaning that they measure all energies that the living animal must make in terms of the Calorie, that is, the large calorie, although as a matter of fact, it is kinetic energy which constitutes the major portion of animal energy made first-hand. Thus, a requirement of 2500 Calories of energy per day would include the kinetic energy (mostly), together with other energies in smaller amounts, that the animal must make within its cells, during a twenty-four-hour period, for normal living.

Fact of conservation of energy. These measured relationships as to energy transformations have led to the discovery of one of the great fundamental facts of physical science: namely, that *the disappearance of a definite quantity of one variety of energy is accompanied by the making of a corresponding quantity of another variety of energy or energies inclusively.*

CHEMICAL ENERGY

In the possession of substances. Chemical energy, as has been suggested previously (p. 76), is in the possession of substances, hidden there because humans have no sense which make them aware of its presence. Furthermore, it is believed not only that *every substance, gram for gram, possesses a fixed supply of chemical energy,* but also that this energy is in part responsible for the nature of the substance. Oxygen, for example, is the substance that it is, with all its distinctive properties, both because it is built of oxygen element, and because, gram for gram, it holds within its keeping a definite quantity of chemical energy. Which, being true, would mean that if the element oxygen, within oxygen substance, were forced to become associated with a greater quantity of chemical energy — made from some other energy — then, at that instant, oxygen substance would have to go out of existence to make a substance possessing more chemical energy. And this is exactly what happens when a charge of electricity is passed through an atmosphere of oxygen, since some of the *electricity is transformed into chemical energy,* as a result oxygen substance involved goes out of existence as ozone is made:

1 gram Oxygen	⟶	1 gram Ozone
↓		↓
possessing a definite quantity of Chemical energy + Electricity	⟶	possessing a larger quantity of Chemical energy

Again, the *substances* carbon, graphite, and diamond, gram for gram, are built of the same element, in this case the element carbon, in the same identical quantities, that is, one gram of carbon element for one gram of each of these substances; nonetheless they are entirely different substances as is evidenced by their different properties:

Carbon	*Graphite*	*Diamond*
solid	solid	solid
black	black	colorless
dull appearance	shiny	very hard
crumbly	soft	crystalline
dry	oily	

What, then, is responsible for making them different substances? And the answer lies, in part, in the fact that, gram for gram, they possess different quantities of chemical energy:

1 gram of Carbon possesses a definite quantity of chemical energy.

1 gram of Graphite has more chemical energy than is possessed by 1 gram of carbon substance.

1 gram of Diamond is in possession of a still greater quantity of chemical energy.

And yet again, in the light of one more example: mercuric oxide is the substance that it is, not only because it is composed of mercury and oxygen elements in a definite weight proportion, but because, gram for gram, this substance holds within its keeping a definite quantity of chemical energy. Therefore, if more chemical energy should be provided, the mercuric oxide would of necessity be obliged to go out of existence to make substances in possession of a larger supply of this energy. And this is what happens when mercuric oxide is heated, inasmuch as some [2] of the *heat* used *is transformed into chemical energy*, consequently, the mercuric oxide decomposes to make the substances mercury and oxygen which between them possess more chemical energy than did the mercuric oxide:

$$\begin{array}{ccc} \begin{array}{c}\text{1 gram}\\ \text{Mercuric oxide}\end{array} & \longrightarrow & \overbrace{\text{Mercury} \quad + \quad \text{Oxygen}}^{\text{1 gram inclusively of these two substances}} \\ \downarrow & & \downarrow \qquad\qquad \downarrow \\ \textit{Chemical energy} + \textit{Heat} & \longrightarrow & \underbrace{\textit{Chemical energy} + \textit{Chemical energy}}_{\text{More chemical energy inclusively than was in the possession of the mercuric oxide.}} \end{array}$$

In like manner, the substances hydrogen, oxygen, chlorine, water, hydrogen chloride, glucose, as well as all other substances, are as they are, not only because of their element composition, but because *given weights of said substances hold within their keeping definite quantities, respectively, of chemical energy.*

Subject to transformation. The fact that *chemical energy, like other energies, is subject to transformations* is by now no new thought. It is, in fact, impossible to get very far with a discussion of this variety of energy without meeting with such transformations, since, as itself, chemical energy cannot be sensed; it is only when this energy is transformed into other energies which can be sensed, that one is able to reason one's way back to the previously existing chemical energy (p. 103).

[2] A portion of the heat used simply raises the temperature of the substances sufficiently to render the reaction appreciable: this portion, therefore, is still heat.

And since chemical energy is in the keeping of substances, it follows that *any energy transformation which involves this variety of energy must be accompanied by a matter transformation* or the going out of existence of previously existing substances and the making of new substances in possession of more or less chemical energy. This is in accordance with the several such studies which have already been undertaken (pp. 95, 96) and will be exemplified again and again in the following studies.

Chemical energy transformed into other energies. It seems reasonable to conclude that when, during a chemical reaction, chemical energy undergoes a transformation into some other variety of energy, it is because the resulting substances contain less chemical energy than the previously existing ones:

$$\begin{array}{ccccc} \overbrace{\text{Substance or Substances}}^{\text{Before the reaction}} & \longrightarrow & \overbrace{\text{Substance or Substances}}^{\text{After the reaction}} & & \\ \downarrow{\scriptstyle\text{Possess}} & & \downarrow{\scriptstyle\text{Possess}} & & \\ \begin{array}{c}\text{Chemical energy in}\\ \text{definite quantity}\end{array} & \longrightarrow & \begin{array}{c}\text{Chemical energy}\\ \text{in less quantity}\end{array} & + & \begin{array}{r}\text{Heat, Light,}\\ \text{Kinetic energy,}\\ \text{or Electricity}\end{array} \end{array}$$

Whether this energy product is heat, kinetic energy, light, or electricity depends in some instances upon the specifically reacting substances, in other instances upon prevailing conditions under which the reactions take place.

Chemical energy into heat. We have already met with a number of reactions (pp. 76 to 77) during which part of the chemical energy in the beginning substance or substances is transformed into heat. Here is another example:

When a jet of hydrogen is brought into contact with oxygen *a little at a time* (p. 84) and kindling temperature is obtained, as these two substances react to make water, part of the *chemical energy* within the oxygen (probably also part within the hydrogen) *is transformed into heat.* These related transformations, matter and energy, are represented briefly thus:

$$\begin{array}{ccccccc} \text{Hydrogen} & + & \text{Oxygen} & \longrightarrow & & & \text{Water}\\ \downarrow & & \downarrow & & & & \downarrow \\ \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & \longrightarrow & \text{Heat} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} \end{array}$$

Chemical energy into kinetic energy. Then there are selected instances when, during the reactions concerned, nature prefers to transform part of the chemical energy possessed by the beginning substance or substances into kinetic energy. Some such instances

of vital concern have been studied previously (p. 79). But once again, *within muscle cells, whenever kinetic energy is in demand for the motion of body parts, nature makes it, mostly, from part of the chemical energy in the keeping of oxygen brought to said cells for that purpose.* Also again, this energy transformation takes place as oxygen reacts with some partner substance already present within the cells. In respect to one such double transformation — matter and energy — the representations are as follows; others should be referred to at this time (p. 79):

$$\begin{array}{ccccccccc}
\text{Glucose} & + & \text{Oxygen} & \longrightarrow & & & \text{Water} & + & \text{Carbon dioxide} \\
\downarrow & & \downarrow & & & & \downarrow & & \downarrow \\
\text{Chemical energy} & + & \text{Chemical energy} & \longrightarrow & \text{Kinetic energy} & + & \text{Chemical energy} & + & \text{Chemical energy}
\end{array}$$

In affairs external to the body, in general, nature transforms *chemical energy into kinetic energy* whenever large quantities of gaseous products are made, all in an instant, *in a confined space,* in which event considerable kinetic energy must be forthcoming for the expansion of these gaseous products as they force their way out against the resistance confronted by the enclosure. In certain instances, as in the blasting of rock masses and in the running of automobiles, man has learned how to put this variety of transformation to his uses. Thus:

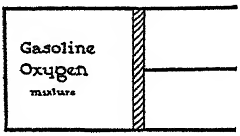


FIG. 26. Kinetic Energy is the Energy Product

When a spark is admitted to the *mixture* of gasoline vapor and oxygen within the cylinders of the automobile, *reaction takes place instantaneously throughout the mixture.* This means that a maximum quantity of two gaseous products, carbon dioxide and water, are made in a confined space, all in a flash of time. Therefore, along with these gases a supply of kinetic energy must also be made for their needed expansions, and nature makes this kinetic energy for the most part from a portion of the chemical energy within the beginning oxygen substance (Fig. 26):

$$\begin{array}{ccccccccc}
\text{Hydrocarbons (of gasoline)} & + & \text{Oxygen} & \longrightarrow & & & \text{Carbon dioxide} & + & \text{Water} \\
\downarrow & & \downarrow & & & & \downarrow & & \downarrow \\
\text{Chemical energy} & + & \text{Chemical energy} & \longrightarrow & \text{Kinetic energy} & + & \text{Chemical energy} & + & \text{Chemical energy}
\end{array}$$

And in this instance the expanding gases set into motion the piston head and the machinery connected therewith. (For interpretation, see p. 77.)

But, unfortunately, most disastrous consequences can also follow from the tendency of nature to make *chemical energy into kinetic energy* for the expansion of shut-in gaseous products. Many a

wrecked stove has followed from just such a happening. And these are the usual conditions: in the oven, a mixture of oxygen from the air with the gaseous reacting partner substances of illuminating gas, which have found their way into this enclosure from the carelessly closed or leaky gas cock; then kindling temperature, provided by the lighted match, for the innocent purpose of "lighting the oven" and — all in an instant — everything is over with save for the possibly sad consequences: a wrecked stove, an injured person, or both!

The same sort of hazard is likewise always present in an operating room in which ethylene, a gaseous anesthetic, is being used and is quite unavoidably mixed with oxygen. Should a spark occur *at any point* to which the mixture has penetrated — from a lighted match or a defective electric fixture — most unfortunate consequences may ensue and for the same reasons already stressed.

Chemical energy into electricity. Then there are selected reactions during which nature chooses to transform chemical energy into electricity. Here is an example:

When strips of zinc and copper are put into dilute sulfuric acid and connected by a conducting wire, electricity is made from chemical energy in one or both of the beginning substances (Fig. 27). The whole truth in respect to this phenomenon involves complications which for our purpose it is quite unnecessary to enter into. The matter and energy transformations concerned are essentially as indicated in the following word equations:

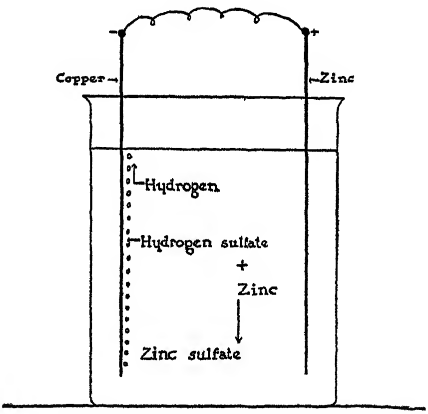


FIG. 27. Electricity is the Energy Product

$$\begin{array}{ccccccccc} \text{Zinc} & + & \text{Hydrogen sulfate} & \longrightarrow & & & \text{Hydrogen} & + & \text{Zinc sulfate} \\ \downarrow & & \downarrow & & & & \downarrow & & \downarrow \\ \text{Chemical energy} & + & \text{Chemical energy} & \longrightarrow & \text{Electricity} & + & \text{Chemical energy} & + & \text{Chemical energy} \end{array}$$

All battery-made electricity is made after this manner. That is, substances are selected whose nature it is to yield up their available *chemical energy* for transformation *into electricity*, rather than into heat or kinetic energy. And it follows that the battery is "run out" or "dead" when all of the beginning substances are gone and

only the product substances remain which hold less chemical energy in their keeping than that which was in the possession of the initial substances.

Other energies transformed into chemical energy. During all reactions of the foregoing study chemical energy is transformed into other energies. However, there are numerous reactions during which the reverse must take place: namely, some other energy — heat, or electricity, or light — must be transformed into chemical energy if reactions are to be rendered possible. Such must obviously be the case when the matter products of the reactions possess more chemical energy than that which is provided within the beginning substances. Some such instances will be the subject of this next study.

$$
\begin{array}{ccccc}
\overbrace{\text{Substance or Substances}}^{\text{Before the reaction}} & & \xrightarrow{\qquad\qquad} & & \overbrace{\text{Substance or Substances}}^{\text{After the reaction}} \\
\Big\downarrow \text{Possess} & & & & \Big\downarrow \text{Possess} \\
\begin{array}{c}\text{Chemical energy in}\\ \text{definite quantity}\end{array} & + & \begin{array}{c}\text{Heat, or light,}\\ \text{or kinetic energy}\\ \text{or electricity}\end{array} & \longrightarrow & \begin{array}{c}\text{Chemical energy in}\\ \text{larger quantity}\end{array}
\end{array}
$$

Heat transformed into chemical energy. There are numerous reactions in which nature seems to prefer to use heat for transformation into needed chemical energy. For example:

Potassium chlorate possesses *less* chemical energy than that which is essential to the oxygen and potassium chloride which can be made from it. Therefore, if this reaction is to take place, *chemical energy must be made from some other variety of energy*, and in this instance nature favors *heat* for such purpose:

$$
\begin{array}{cccccc}
\text{Potassium chlorate} & & \xrightarrow{\qquad\quad} & \text{Oxygen} & + & \text{Potassium chloride} \\
\downarrow & & & \downarrow & & \downarrow \\
\begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + \ \text{Heat} & \longrightarrow & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array}
\end{array}
$$

Interpreted: As potassium chlorate decomposes to make the substances oxygen and potassium chloride, some of the heat used is transformed into the extra amount of chemical energy that is essential to the oxygen (chiefly) and to potassium chloride (to some extent) over and above the chemical energy that was provided by the beginning substance, potassium chlorate.

The same sort of an accounting holds as to the necessity for using heat in order to accomplish the decomposition of mercuric oxide (p. 96). And there are numerous other reactions, in which nature favors the use of heat for transformation into the added amount of chemical energy necessary to the resulting substances over and above that provided within the beginning substances.

Electricity into chemical energy. There are other instances when electricity lends itself most happily for transformation into the required extra chemical energy for the substance products of a reaction. Two examples of such reactions are: the making of ozone from oxygen (p. 95), and the decomposition of water to make hydrogen and oxygen (p. 20):

$$\begin{array}{ccccccc} \text{Water} & & & \longrightarrow & \text{Oxygen} & + & \text{Hydrogen} \\ \downarrow & & & & \downarrow & & \downarrow \\ \text{Chemical energy} & + & \text{Electricity} & \longrightarrow & \text{Chemical energy} & + & \text{Chemical energy} \end{array}$$

Interpreted: As water decomposes to make oxygen and hydrogen, electricity is transformed into the added amount of chemical energy that these new substances must have over and above the chemical energy which was present in the beginning water.

Light into chemical energy. But sometimes nature chooses light for transformation into chemical energy. This is the case in that most important of all reactions which has been presented previously (p. 66): namely, the reaction between water and carbon dioxide in the chlorophyll-containing cells of plants. During this reaction light is transformed into the requisite quantity of chemical energy that oxygen (for the most part) and plant carbohydrates (perhaps to a limited extent) must have over and above that provided within the initial carbon dioxide and water:

$$\begin{array}{ccccccccc} \text{Water} & + & \text{Carbon dioxide} & & & \longrightarrow & \text{Oxygen} & + & \text{Carbohydrate} \\ \downarrow & & \downarrow & & & & \downarrow & & \downarrow \\ \text{Chemical energy} & + & \text{Chemical energy} & + & \text{Light} & \longrightarrow & \text{Chemical energy} & + & \text{Chemical energy} \end{array}$$

This brings us to another reason (p. 81) why this reaction is of such great significance in world concerns, since herein lies the means whereby *great quantities of the energy of the sun are captured by earth and imprisoned as chemical energy within oxygen substance,* later to be transformed (1) into kinetic energy and other energies within the body cells as oxygen reacts with one or another of the partner substances provided therein; (2) or into heat and kinetic energy outside the body, once again, as oxygen is brought into reaction with various substances selected for such purpose.

Measurement of chemical energy. There are three factors of prime importance in regard to the measurement of chemical energy. *First:* it cannot be measured directly, but must be transformed into heat or some energy which can be measured. And, quite logically, the quantity of heat or kinetic energy obtained

would, by reasoning backwards, become a measure of that which *was* chemical energy before the transformation took place. *Second:* even then only a portion of the chemical energy of the beginning substance or substances is available for measurement, because some must remain chemical energy within the resulting substances. *Third:* in many instances it is not possible to arrive at a measurement of the available chemical energy in one substance all by itself, in that said substance may yield up part of its chemical energy for transformation only in reaction with another substance, in which case one would be finding a measure for the *available chemical energy of the two substances* inclusively.

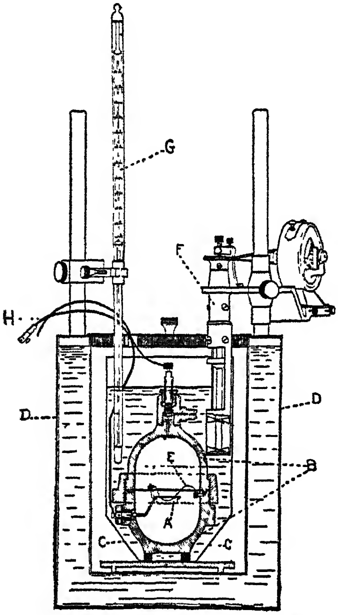


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FIG. 28. Diagram of Bomb Calorimeter with Bomb in Position

A. Platinum dish holding food sample.
B. Bomb filled with pure oxygen enclosing food sample.
C. Can holding water, in which bomb is submerged.
D. Outer double-walled insulating jacket.
E. Fuse, which is ignited by an electric current.
F. Motor-driven water stirrer.
G. Thermometer.
H. Electric wires to send current through fuse.

One method that is used for measuring the available chemical energy of a substance, or substances inclusively, applies when *heat* can be obtained as the energy product. The essence of the method[3] is as follows: weighed quantities of the substance or substances concerned are made to react in a closed container which is buried in water (Fig. 28). This portion of the apparatus is, in turn, enclosed in a double-walled, heat-insulating jacket. The heat product is thereby collected in the water and can be measured, providing the weight quantity of the water has been previously noted and the temperature of the water was taken before the reaction began and is taken again when it is complete. This heat, then, becomes a measure: (1) of the energy product obtainable from the reaction of given quantities of the be-

[3] Details of procedure can be obtained from any comprehensive text on nutrition.

ginning substances; hence, (2) of the available chemical energy previously in the possession of said substances. For example:

1. When *1 gram of sodium and 1.54 grams of chlorine* (which are sufficient quantities so that there will be no excess of either substance left) are the reacting substances within such a calorimeter, sufficient heat is made to raise the temperature of 2 Kg. of water through 2.12° C. or 4.24 Calories. Moreover, 4.24 Calories is the quantity of energy product that can always be expected from reaction of these quantities of these two substances; hence this 4.24 Calories must be a measure of the available chemical energy possessed by 1 gram of sodium and 1.54 grams of chlorine.

2. Again, it has been determined, through the agency of such a piece of apparatus, that when *1 gram of carbon and 2.66 grams of oxygen* react to make carbon dioxide, enough heat is made to raise the temperature of 2 Kg. of water through 3.93° C., or 7.86 Calories. And this is the quantity of energy product always made from this reaction between these quantities of these substances; consequently, 7.86 Calories becomes a measure of the available chemical energy possessed inclusively by 1 gram of carbon and 2.66 grams of oxygen; and most of this is in the possession of the oxygen.

Thus, in general, the quantity of energy product obtained becomes a measure of the available chemical energy previously possessed by the beginning substance or substances. And vice versa, the available chemical energy possessed by a substance, or substances inclusively, determines the quantity of energy product that will be made whenever said substances engage in reaction.

Findings as to the quantities of available chemical energy possessed by oxygen and various partner substances, arrived at experimentally after the foregoing method, are as follows:

1 gram of sulfur and..........	.998 gram of oxygen	2.347 Calories
1 gram of glucose and........	1.066 grams of oxygen	3.75 Calories
1 gram of methyl alcohol and..	1.5 grams of oxygen	5.33 Calories
1 gram of ethyl alcohol and....	2.085 grams of oxygen	7.11 Calories
1 gram of carbon and.........	2.66 grams of oxygen	7.865 Calories
1 gram of stearin (a fat) and...	2.9 grams of oxygen	9.45 Calories (about)
1 gram of acetylene and......	3.075 grams of oxygen	11.99 Calories
1 gram of methane and.......	3.9 grams of oxygen	13.14 Calories
1 gram of hydrogen and......	7.93 grams of oxygen	28.68 Calories

Questions

1. Mention several processes of ordinary occurrence during which one variety of energy is transformed into another variety of energy.

2. How much is a small calorie of heat? A large calorie? Which of these is the measuring unit used by the nutritionist?

3. State the fact of conservation of energy.

4. How much electricity would be used (providing no waste occurs) to raise the temperature of 1 Kg. of water from 20° C. to 100° C.?

5. How many grams of oxygen must be taken in by the muscle cells concerned for reaction with glucose to make sufficient energy for carrying a person weighing 100 lbs. up a flight of stairs 15 ft. high? How much glucose must become involved?

6. Why must there be an energy product when the celluloses of wood react with oxygen? What is the chief source of this energy product? Represent the related matter and energy transformations by means of word equations.

7. Why must heat be used to make the decomposition of mercuric oxide possible? What becomes of this heat?

8. Assuming the component substances of illuminating gas to be hydrogen, carbon monoxide, and methane: represent in word equation form the related matter and energy transformations for the three reactions that take place in the burning of this mixture of gaseous substances.

9. Criticize the statement "Gasoline is highly explosive." Give accurate statements which will make clear the conditions that must be met for an explosion to occur involving this material.

10. Which contains more chemical energy:
  a. Water or the hydrogen and oxygen (inclusively) which result from its decomposition? Give reason.
  b. The component substances of a "live" battery or the substances remaining in a "dead" battery? Give reason.
  c. Cane sugar or the various substances (inclusively) resulting from its decomposition? Give reason.

11. Represent by means of word equations the related matter and energy transformations that take place within the cells when:
  a. One gram of glucose reacts with oxygen.
  b. One gram of stearin (a typical fat) reacts with oxygen.

In each instance indicate how much oxygen would engage in the reaction, and how much energy product would result. What is the source of the energy product?

12. Interpret the word equations for related matter and energy transformations:
  a. For the reaction between oxygen and hydrocarbons of gasoline, as given on p. 77 (2). As given on p. 98. Account for any difference.
  b. For reaction between oxygen and fats, as given on p. 79. What difference would there be if this reaction were to take place in a calorimeter?
  c. For the reaction during which: (1) ozone is made from oxygen, as given on p. 95; (2) mercuric oxide undergoes decomposition, as given on p. 96.
  d. For reaction between glucose and oxygen within muscle cells, as given on p. 98.
  e. For reaction between water and carbon dioxide in chlorophyll cells of plants, as given on p. 101.

13. Account for the possible wrecking of the stove as a result of reaction described on p. 98.

14. Study the data provided on p. 103; this table lists a typical selection of reaction possibilities involving oxygen. What do you observe regarding the relationship between quantities of oxygen that participate in the various reactions and the quantities of energy products made? What significance do you see in this relationship?

CHAPTER IX

Chemical Measurings and Related Beliefs

Very early in chemistry history it was found desirable to obtain means for carrying on measurings from a chemical view-point: for measuring quantities of substances as they become involved in chemical reactions, and for measuring quantities of elements that are built into substances. And after a great deal of careful quantitative research, such measurings have been obtained.

It is impossible in this brief text to enter into the experimental studies through which scientists have arrived at the very useful discoveries made in this connection, but we can be introduced to some of their findings and learn how to make use of them.

SUBSTANCES AND CHEMICAL REACTIONS

The measurement of substances as they become involved in chemical reactions. Significant weights, one for each substance, have been discovered which, although frequently awkward in

Aluminium	26.97	Mercury	200.61
Aluminium oxide	101.94	Mercuric oxide	216.61
Ammonia	62.008	Nitrogen	28.016
Carbon dioxide	44.01	Oxygen	32.
Chlorine	70.914	Potassium chlorate	122.553
Copper	63.57	Potassium chloride	74.553
Glucose	180.156	Water	18.016
Hydrogen	2.016	Wood alcohol	32.042
Hydrogen chloride	36.465	Zinc	65.38
Iron	55.84	Zinc chloride	136.294
Methane	16.042		

themselves, function as measuring units in respect to the quantities of substances that become involved in chemical reactions. Examples of some of these values for substances specified are given in the above table.

Molecular weights and their functioning. The label that has come to be applied to these numerical values is *molecular weights* of substances, but a more significant label would be unit-reacting-weights, since it is a fact that *substances enter into and are made from chemical reactions in whole number multiples of their molecular*

weights. Accordingly, the substance oxygen engages in reactions in one times, two times, or always in whole numbers times 32 parts by weight; the substance water engages in reactions in one times, two times, or always in whole numbers times 18.016 parts by weight.

But let us study the functioning of these weight units by means of specific reactions, referring to the foregoing table of molecular weights for the unit reacting weights of the participating substances. Thus:

$$\begin{array}{ccccc} \text{Potassium chlorate} & \longrightarrow & \text{Oxygen} & + & \text{Potassium chloride} \\ 2 \times \underline{122.553} & & 3 \times \underline{32} & & 2 \times \underline{74.553} \end{array}$$

Interpreted. In general terms: 2 × 122.553 parts by weight of potassium chlorate decompose to make 3 × 32 parts by weight of oxygen and 2 × 74.553 parts by weight of potassium chloride.

More specifically: with measurements made in grams, 2 × 122.553 grams of potassium chlorate decompose to make 3 × 32 grams of oxygen and 2 × 74.553 grams of potassium chloride.

Other reactions showing the functioning of molecular weights as unit reacting weights for substances are represented as follows, but without interpretations:

$$\begin{array}{ccccc} \text{Mercuric oxide} & \longrightarrow & \text{Oxygen} & + & \text{Mercury} \\ 2 \times \underline{216.61} & & 1 \times \underline{32} & & 2 \times \underline{200.61} \end{array}$$

$$\begin{array}{ccccccc} \text{Methane} & + & \text{Oxygen} & \longrightarrow & \text{Water} & + & \text{Carbon dioxide} \\ 1 \times \underline{16.042} & & 2 \times \underline{32} & & 2 \times \underline{18.016} & & 1 \times \underline{44.01} \end{array}$$

$$\begin{array}{ccccc} \text{Hydrogen} & + & \text{Oxygen} & \longrightarrow & \text{Water} \\ 2 \times \underline{2.016} & & 1 \times \underline{32} & & 2 \times \underline{18.016} \end{array}$$

$$\begin{array}{ccccccc} \text{Aluminium} & + & \text{Water} & \longrightarrow & \text{Hydrogen} & + & \text{Aluminium oxide} \\ 2 \times \underline{26.97} & & 3 \times \underline{18.016} & & 3 \times \underline{2.016} & & 1 \times \underline{101.94} \end{array}$$

$$\begin{array}{ccccccc} \text{Zinc} & + & \text{Hydrogen chloride} & \longrightarrow & \text{Hydrogen} & + & \text{Zinc chloride} \\ 1 \times \underline{65.38} & & 2 \times \underline{36.468} & & 1 \times \underline{2.016} & & 1 \times \underline{136.294} \end{array}$$

Thus it appears that, as to any reaction, once both the molecular weights and the whole number molecular weight multiples for substances concerned are obtained, the quantitative story thus told becomes an expression: (1) of the *weight relationship* that must be met on the part of the substances mutually participating in the reaction, or (2) of actual concrete quantities of said participating substances if *gram molecular weights* are employed or molecular weights on any other weighing basis such as *pound molecular weights.*

From now on, then, and most emphatically, the student must continually bear in mind that these measurings discussed thus far are *factual*, since the *molecular weight of a substance is a very real weight value that serves as a measuring unit for the substance in chemical reactions.*

The source of molecular weights. Molecular weights of many substances are the actual or calculated weights in grams of 22.4 liters of the substances in the gaseous state at 0° C. and under a pressure equal to that exerted by a column of mercury 760 mm. high. Just why weights thus obtained constitute unit reacting weights for substances will not be taken up in this study; for more information in this connection the student is referred to more comprehensive texts on inorganic chemistry.

A question. And now comes the question as to why it is that substances become quantitatively involved in chemical reactions in whole number multiples of their molecular weights?

The real answer to this question must be that no one really knows. But a significant theory has been developed which supplies assumptions that fit in very neatly with the facts, so neatly indeed, that believing chemists feel certain that imagined conditions lie pretty close to reality.

Two basic assumptions. The *first assumption* claims that *every substance is made up of minute ultimate particles* of said substance. There are spaces between these particles, so that they do not touch each other, and the particles themselves are so ultra-tiny that it is impossible to render them visible to the eye even with the aid of the highest powered microscope. The label that has been given to these believed-in ultimate particles of substances is *molecules.*

The second assumption claims that molecules of the same substance are exactly alike in all respects, while those of different substances are different as to each other.[1]

Applying these two assumptions to specific substances, it is believed that the smallest visible drop of water is composed of millions of molecules of water which are exactly alike — identical structure, size, weight (Fig 29). Or if the substance is carbon, then every tiniest, visible speck of carbon is supposedly composed of millions of these ultimate bits or molecules of carbon (Fig. 30), which are identical as to each other in every way. Or if the substance is hydrogen, then every portion presumably includes millions of molecules of hydrogen which would look exactly

[1] Recent experimental findings have led to modifications of some of these assumptions. But for the present the assumptions as originally conceived will serve best the immediate purpose.

alike if one could see them, would weigh the same, and would behave alike in chemical ways (Fig. 31).

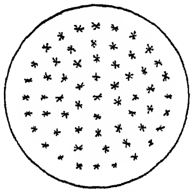


FIG. 29

A drop of *water* made up of myriads of *molecules of water.*

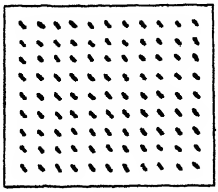


FIG. 30

A speck of *carbon* composed of millions of *molecules of carbon.*

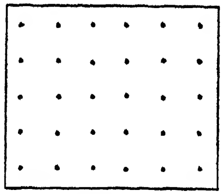


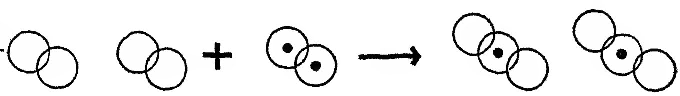
FIG. 31

A small portion of *hydrogen* composed of millions of *molecules of hydrogen.*

Why the whole number molecular weight involvement of substances in reactions? We are now in a position to find an answer to this question, since it is believed that it is because in the ultimate unit reaction — that is, the least possible engagement as to their molecules — substances enter into and are made from reactions in whole numbers of molecules. And the large quantity reaction, such as molecular weight involvements of the substances, is the result millions of times repeated of this ultimate unit engagement among their molecules. For example:

	2 Hydrogen	+	1 Oxygen	⟶	2 Water
Factually in large quantities	2 molecular weights of hydrogen	react with	1 molecular weight of oxygen	to make	2 molecular weights of water
because					
Theoretically in the ultimate molecule line-up	2 molecules of hydrogen	react with	1 molecule of oxygen	to make	2 molecules of water

Pictured representation



Functions of the whole number reacting ratio. It follows from the foregoing that the whole number reacting ratio as to a chemical reaction tells not only, *factually*, the number of molecular weights of the substances that are mutually concerned in the large quantity reaction, but also, *theoretically*, the number of molecules of the substances that are believed to become engaged in the ultimate unit reaction.

A third assumption. Molecular weights of substances on the same weighing basis (i.e. grams, ounces, pounds, etc.) are believed to include the same numbers of molecules of said substances: if *gram molecular weight* of the substance is the weight involved, the number of molecules included therein is believed to be 6.06×10^{23} molecules[2] of the substance. Thus:

32 grams of oxygen are believed to include 6.06×10^{23} molecules of oxygen.
18.016 grams of water are believed to include 6.06×10^{23} molecules of water.
Gram molecular weight of any substance includes 6.06×10^{23} molecules of the substance.

Why does each substance have its own fixed molecular weight? And according to the foregoing assumptions the answer must be: (*fact*) each substance has its own specific molecular weight because, (*theory*) the molecular weight of a substance always includes a definite number of constant weight molecules of the substance, the inclusive weight of which must be peculiar to the substance since the weight of the single molecule is peculiar to said substance. Hence:

Fact	*Theory*
32 is this fixed weight for oxygen.....	because on any given weighing basis such as grams this weight includes a definite number of constant weight molecules of oxygen.
18.016 is this fixed weight for water....	because it includes a definite number of constant weight molecules of water.

Relative weights of molecules. Following upon the acceptance of the foregoing assumptions, various interesting speculations in regard to molecules have become possible; among these are speculations as to the actual weights of molecules of substances, and the relative weights of molecules of substances in respect to each other. But since actual weights of molecules are infinitesimally small, their *relative weights* are the values which are usually taken into consideration.

So, with the foregoing assumptions in mind, it seems reasonable to conclude that the weights of single molecules of various substances must be to each other as are the weights of equal numbers of molecules of the substances, hence as are the molecular weights of said substances. For example:

$$\left.\begin{array}{c}\text{the weight}\\ \text{of}\\ \text{one molecule}\\ \text{of}\\ \text{hydrogen}\end{array}\right\}\begin{array}{c}\text{is}\\ \text{to}\end{array}\left\{\begin{array}{c}\text{the weight}\\ \text{of}\\ \text{one molecule}\\ \text{of}\\ \text{oxygen}\end{array}\right\}\begin{array}{c}\text{is}\\ \text{to}\end{array}\left\{\begin{array}{c}\text{the weight}\\ \text{of}\\ \text{one molecule}\\ \text{of}\\ \text{water}\end{array}\right\}\text{ as } 2.016 : 32 : 18.016$$

since 2.016 grams of hydrogen, 32 grams of oxygen, and 18.016 grams of water include the same number of molecules, and weights of single molecules of hydrogen, oxygen, and water are to each other as are the weights of equal numbers of molecules of these substances.

[2] $6.06 \times 10^{23} = 606{,}000{,}000{,}000{,}000{,}000{,}000{,}000$.

ELEMENTS WITHIN SUBSTANCES

Atomic weights as units for elements within molecular weights of substances. Inasmuch as unit quantities of substances, from a chemical angle, are their molecular weights, it seems logical that measurements as to elements as they are combined within substances should be in reference to quantities of elements that are combined within the molecular weights of substances. And it has been discovered that nature follows a very definite pattern in this respect, since the facts are:

1. *There is a fixed weight for each element, called its atomic weight, which is the least weight of the element that is present in combination within molecular weights of all substances containing it.*

2. *Furthermore, the atomic weight is a unit combining weight because the element is combined within molecular weights of all substances containing it in whole number multiples of this weight.*

Atomic weights of elements

Aluminium	26.97
Barium	137.36
Calcium	40.08
Carbon	12.01
Chlorine	35.457
Copper	63.57
Hydrogen	1.008
Iron	55.84
Magnesium	24.32
Nitrogen	14.008
Oxygen	16.
Phosphorus	30.98
Potassium	39.096
Sodium	22.997
Sulfur	32.06
Zinc	65.38

Some of these weight values for the elements concerned are given in the accompanying table (see also the back cover of this text); and the composition of a few substances, as given below, will show how atomic weights function:

$$\underbrace{\overset{\text{Hydrogen}}{2 \times \underline{1.008}} \quad \overset{\text{oxide}}{1 \times \underline{16}}}_{\text{Molecular weight}} \qquad \underbrace{\overset{\text{Potassium}}{1 \times \underline{39.096}} \quad \overset{\text{chlor}}{1 \times \underline{35.457}} \quad \overset{\text{ate}}{3 \times \underline{16}}}_{\text{Molecular weight}}$$

$$\underbrace{\overset{\text{Carbon}}{1 \times \underline{12.01}} \quad \overset{\text{dioxide}}{2 \times \underline{16}}}_{\text{Molecular weight}} \qquad \underbrace{\overset{\text{Hydrogen}}{1 \times \underline{1.008}} \quad \overset{\text{chloride}}{1 \times \underline{35.457}}}_{\text{Molecular weight}}$$

$$\underbrace{\overset{\text{Hydrogen}}{2 \times \underline{1.008}} \quad \overset{\text{sulf}}{1 \times \underline{32.06}} \quad \overset{\text{ate}}{4 \times \underline{16}}}_{\text{Molecular weight}} \qquad \underbrace{\overset{\text{Magnesium}}{1 \times \underline{24.32}} \quad \overset{\text{chloride}}{2 \times \underline{35.457}}}_{\text{Molecular weight}}$$

A study of the above will show, for example, that within molecular weights of substances the element oxygen is combined in whole numbers times its atomic weight of 16; the element hydrogen in whole numbers times its atomic weight of 1.008; the element chlorine in whole numbers times its atomic weight of 35.457.

So it is that, if the number of atomic weights of the elements within the molecular weight of any given compound is known, one is in a position to anticipate the quantitative composition of said compound. For example:

The number of atomic weights of sodium, phosphorus, and oxygen in the molecular weight of sodium phosphate	Sodium 3 atomic weights	phosph 1 atomic weight	ate 4 atomic weights
The molecular weight computed	Sodium $3 \times \underline{22.997}$	phosph $1 \times \underline{30.98}$	ate $4 \times \underline{16}$
	163.971 (molecular weight)		

Therefore, the whole story as to the composition of this compound is revealed. Thus:

In general terms: 163.971 parts by weight of sodium phosphate is composed of 3 × 22.997 parts by weight of sodium, 1 × 30.98 parts by weight of phosphorus, and 4 × 16 parts by weight of oxygen.

Or in specific quantities, in grams: 163.971 grams of sodium phosphate is composed of 3 × 22.997 grams of sodium, 1 × 30.98 grams of phosphorus, and 4 × 16 grams of oxygen.

Another question. These findings lead naturally to another question: namely, why are elements combined within molecular weights of substances in whole number multiples of their atomic weights? And again, it is necessary to turn to theory for the answer and to certain believed-in conditions that conform so nicely with the facts which they serve to explain that the theories have come to be accepted as though they were known to be true.

This is theory. We are already familiar with the belief that the ultimate particles of substances are their molecules. Further imaginings lead one to within the molecules and the way elements may be built therein.

Basic assumptions. *First.* Elements are presumably present within molecules of substances as exceedingly minute, ultimate particles of said elements called *atoms*. For examples see Figures 32 to 35.

Second assumption. Atoms of the same element have their own characteristic and constant weight.[3] That is:

All atoms of hydrogen weigh the same whether within molecules of hydrogen the substance, molecules of water, or molecules of other substances. All atoms of oxygen have their own peculiar weight whether within molecules of

[3] As a result of recent experimental findings, this assumption has undergone modification to: atoms of the same element have the same *average weight*.

water or molecules of carbon dioxide. Moreover, when atoms of hydrogen or atoms of oxygen leave given molecules to enter into those of another substance they carry their own peculiar weights along with them.

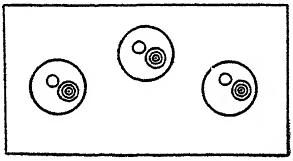


FIG. 32. Each Molecule of Hydrogen Chloride is Composed of 1 Atom of Hydrogen and 1 Atom of Chlorine.

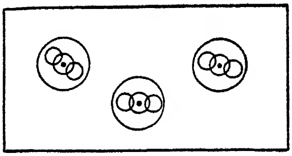


FIG. 33. Each Molecule of Water is Composed of 2 Atoms of Hydrogen and 1 Atom of Oxygen.

Third assumption. Atoms of various elements have the same definite combining capacities for atoms of other elements under the same conditions of combination. Thus:

Under conditions in which molecules of water are made, always two atoms of hydrogen are combined with one atom of oxygen (Fig. 33); hence molecules of water are all alike. Again, under conditions in which molecules of sulfur dioxide are made within each molecule one atom of sulfur is combined with two atoms of oxygen (Fig. 34); hence molecules of sulfur dioxide are all alike. But under other conditions, those in which molecules of sulfur trioxide are made, one atom of sulfur is found combined with three atoms of oxygen within each molecule (Fig. 35).

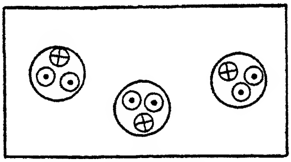


FIG. 34. Each Molecule of Sulfur Dioxide is Composed of 1 Atom of Sulfur and 2 Atoms of Oxygen.

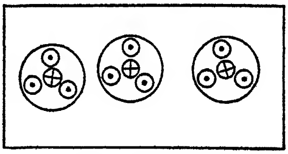


FIG. 35. Each Molecule of Sulfur Trioxide is Composed of 1 Atom of Sulfur and 3 Atoms of Oxygen.

Why are elements combined within molecular weights of substances in whole number multiples of their atomic weights? This is the question (p. 111) that called for the foregoing theory and here is the answer. It is believed that the whole numbers of atomic weights of elements within the molecular weight of a substance are determined by the numbers of whole constant weight atoms of the elements that are combined within each of the exactly alike molecules, many millions of which comprise the molecular weight of said substance. Accordingly:

Example one. *Fact:* one molecular weight of water, or its large unit quantity, is composed of 2 atomic weights of hydrogen and 1 atomic weight of oxygen; because, *theory:* presumably, each molecule of water is composed of 2 atoms of hydrogen and 1 atom of oxygen.

Example two. Fact: one molecular weight of hydrogen sulfate (p. 110), or its large unit quantity, is composed of 2 atomic weights of hydrogen, 1 atomic weight of sulfur, and 4 atomic weights of oxygen; because, *theory:* presumably each molecule of hydrogen sulfate is composed of 2 atoms of hydrogen, 1 atom of sulfur, and 4 atoms of oxygen.

Double functioning of the whole number combining ratio. It follows from the foregoing study that with the whole number multiples given as to the quantities of elements that are combined within a substance, a key is thereby provided: *factually,* as to the number of atomic weights of elements that are known to be combined within the molecular weight of the substance; and *theoretically,* as to the number of atoms of the elements that are believed to be combined with each other within the molecule of said substance.

Atomic theory continued. Another assumption of the atomic theory is the belief that atomic weights of various elements include the same number of atoms of the elements, distributed, of course, within molecules of substances. For example:

If one could pick out, from molecules of substances, enough hydrogen atoms to weigh inclusively 1.008 grams, enough oxygen atoms to weigh 16 grams, enough chlorine atoms to weigh 35.457 grams — one would be dealing with the same number of atoms of these elements.

Relative weights of atoms. It follows, then, that since all atoms of the same element have the same weight while atoms of different elements have different weights, and since atomic weights of elements include equal numbers of atoms — the relative weights of single atoms of the various elements must be to each other as are the atomic weights of the elements. Thus:

$$\left.\begin{array}{c}\text{the weight}\\ \text{of}\\ \text{one atom}\\ \text{of}\\ \text{hydrogen}\end{array}\right\}\text{ is to }\left\{\begin{array}{c}\text{the weight}\\ \text{of}\\ \text{one atom}\\ \text{of}\\ \text{chlorine}\end{array}\right\}\text{ is to }\left\{\begin{array}{c}\text{the weight}\\ \text{of}\\ \text{one atom}\\ \text{of}\\ \text{oxygen}\end{array}\right\}\text{ as } 1.008 : 35.457 : 16$$

In fact, another definition of atomic weight that is frequently given is: atomic weight is the relative weight of the atom of an element. This definition, however, is in reference to a *theoretical* unit; the other definition (p. 110) is in reference to an *actual* unit.

SUMMARY

As to elements within substances. *Fact.* The atomic weight of an element is a fixed weight that is peculiar to each element; it is the least weight of the element found combined within molecular weights of substances containing it. It is a unit combining weight because the element is combined within molecular weights of substances in whole number multiples of its atomic weight.

Theory. 1. The atom is the infinitesimal, ultimate particle of an element. Atoms of elements are always combined with each other within molecules of substances. Atoms of each element have their own peculiar and constant weight.

2. Weights of single atoms of the various elements are to each other, relatively, as are the atomic weights of said elements.

As to substances. *Fact.* The molecular weight of a substance is a fixed weight that is peculiar to the substance. It is a unit reacting weight since a substance participates in chemical reactions in whole number multiples of its molecular weight.

Theory. 1. The molecule is the infinitesimal and ultimate particle of a substance with its own fixed weight.

2. The gram molecular weight of every substance includes 6.06×10^{23} molecules of the substance.

3. Weights of single molecules of various substances are to each other, relatively, as are the molecular weights of said substances.

As to the composition of substances. The whole number multiples as to elements within substances tell:

Factually: in large quantity measurements, the number of atomic weights of the elements that are known to be combined within the molecular weight of the substance.

Theoretically: the number of atoms of the elements that are believed to be combined with each other within each molecule of the substance.

As to substances and chemical reactions. The whole number multiples as to substances involved in a reaction tell:

Factually: in large quantity measurements, the number of molecular weights of the several substances mutually involved in the reaction.

Theoretically: the number of molecules of the several substances believed to be involved in the ultimate unit reaction.

Questions

1. What is the function of molecular weights? Of atomic weights?

2. Why does 2.016 constitute the molecular weight of hydrogen whereas 44.01 is the molecular weight of carbon dioxide?

3. a. What are the basic assumptions relating to molecules?
   b. How many molecules are believed to be contained within 44.01 grams of carbon dioxide? 18.016 grams of water? 2.016 grams of hydrogen?
   c. What are the relative weights of single molecules of carbon dioxide, water, and hydrogen? Give reasons.

4. The following are whole number reacting multiples for the substances concerned in the reactions specified:

a. Supply molecular weights (table, p. 105) and interpret (1) in grams, (2) in general terms.

b. Interpret in molecule terms.

Hydrogen	+ Nitrogen	⟶ Ammonia
3	1	2

Wood alcohol	+ Oxygen	⟶ Water	+ Carbon dioxide
2	3	4	2

5. Why is 16 the atomic weight of oxygen? 14.008 the atomic weight of nitrogen? 40.08 the atomic weight of calcium?

6. What are the basic assumptions of the atomic theory?

7. What are the comparative weights of atoms of the following elements: carbon, hydrogen, oxygen, and iron? (See table, p. 110.)

8. The following are whole number atomic weight multiples as to the elements within molecular weights of the following substances:

a. Compute the molecular weights of the substances.

b. Tell what quantitative information is thereby provided concerning the composition of the substance: (1) in grams, (2) in general terms:

Calcium carbonate
1 1 3

Mercuric chloride
1 2

Nitrogen (substance)
2

c. What is the presumed composition of the molecule of each of these substances?

CHAPTER X

Shorthand for Chemical Measurings

IN RESPECT OF ELEMENTS

Symbols for atomic weights of elements. The first discoverers in the early 1800's of *atomic weights* for such elements as were then known were John Dalton, an Englishman, and Jöns Berzelius of Sweden. And along with their findings came the desire to represent these experimentally determined, but awkward, values in some significant shorthand manner. Berzelius decided that these devices should suggest the names of the elements; Dalton thought that distinctive characters should be devised towards such end. Thus:

The element	*Atomic weight*	*Berzelius' suggestions*	*Dalton's suggestions*
Carbon....................	12.01	C	●
Chlorine..................	35.457	Cl	
Hydrogen.................	1.008	H	○
Nitrogen..................	14.008	N	⦶
Oxygen....................	16.	O	⊙
Sulfur.....................	32.06	S	⊕

But Berzelius claimed that such characters as Dalton was suggesting and using "disfigured the page." Dalton, on the other hand, called Berzelius' characters "horrifying," claiming that they would be confused with abbreviations merely for the names of elements without regard to their quantitative significance. It was the idea of Berzelius that continued to be used by scientists as more and more elements and their atomic weights were discovered.

So today the adopted shorthand character, or symbol as it is called, for the atomic weight of an element is the first letter (capitalized), or the first letter (capitalized) and some other significant letter (not capitalized), of the English or Latin name for the element. A partial list of elements and their atomic weights together with the symbols that represent them are given in the following table. A more extensive list is to be found on the back cover of this text.

The element	*Its atomic weight*	*Symbol for atomic weight*	*Symbol for the atom*
Barium	137.36	Ba	Ba
Carbon	12.01	C	C
Calcium	40.08	Ca	Ca
Chlorine	35.457	Cl	Cl
Copper (Cuprum)	63.57	Cu	Cu
Hydrogen	1.008	H	H
Iron (Ferrum)	55.85	Fe	Fe
Lead (Plumbum)	207.21	Pb	Pb
Magnesium	24.32	Mg	Mg
Mercury (Hydrargyrum)	200.61	Hg	Hg
Nitrogen	14.008	N	N
Oxygen	16.	O	O
Phosphorus	30.08	P	P
Potassium (Kalium)	39.096	K	K
Silver (Argentium)	107.88	Ag	Ag
Sodium (Natrium)	22.997	Na	Na
Sulfur	32.06	S	S
Tin (Stannum)	118.7	Sn	Sn
Zinc	65.38	Zn	Zn

Symbols for atoms of elements. Another and more restricted use that is made of symbols is for representing *atoms* of elements. This use is also exemplified in the above table.

The use of symbols. The simple functioning of symbols is apparent, since (1) a symbol can be set down instead of the *atomic weight*, which more times than not is awkward in itself, to be translated into the actual atomic weight value of the element when one so desires; (2) or, if one is dealing with the *atom*, then the symbol can be set down to represent the same. Accordingly:

The symbol C can be set down to represent	12.01 parts by weight of the element carbon or 12.01 grams of carbon or the atomic weight of carbon on any other weighing basis.

Theoretically, the symbol C can be set down to represent one atom of the element carbon.

Symbols appear collectively. Another important item concerning symbols is that usually they appear collectively. This is because *factually*, two or more atomic weights of elements are found combined with each other within molecular weights of substances; while *theoretically*, two or more atoms of elements are combined with each other within molecules. For example:

NaOH is an assemblage of symbols which tells its own story as follows:

Factually, it tells that one molecular weight of sodium hydroxide
contains 1 atomic weight or 22.997 parts by weight of sodium
1 atomic weight or 16 parts by weight of oxygen
1 atomic weight or 1.008 parts by weight of hydrogen

Theoretically, NaOH tells that each molecule of sodium hydroxide
contains 1 atom of sodium
1 atom of oxygen
1 atom of hydrogen

But this really anticipates our next study.

SHORTHAND IN RESPECT OF SUBSTANCES

Formulas for molecular weights of substances. Since elements are present in the molecular weight of a substance in whole number multiples of their atomic weights, it should be possible to represent the composition of said molecular weight through the same whole number multiple assemblage of the symbols for the atomic weights of the elements concerned. Thus:

1. The substance	Hydrogen chloride	
Atomic weights of elements and multiples. .	1 × 1.008	1 × 35.457
Or, in general	1 atomic weight	1 atomic weight
Atomic weights represented by symbols. .	1 H	1 Cl
Formula for molecular weight as it usually appears.......	HCl	

2. The substance	Hydrogen sulfate		
Atomic weights of elements and multiples....	2 × 1.008	1 × 32.06	4 × 16
Atomic weights represented by symbols......	2 H	1 S	4 O
Formula for molecular weight as it usually appears.........	H_2SO_4		

3. The substance..	Oxygen
Atomic weight of oxygen element and multiple.................	2 × 16
Atomic weight of oxygen represented by its symbol............	2 O
Formula for molecular weight of oxygen substance................	O_2

Hence the *formula* is a shorthand device for representing the composition of the molecular weight of a substance.

Formulas for molecules of substances. Then there is the other use for the formula, with a purely *theoretical* significance, for representing the composition of the molecule of the substance, which is in accordance with the other use of the symbol for representing the atom of the element.

These two uses for formulas are contrasted in the following examples:

1. H_2O is the *formula for the molecular weight* of water with H and O as symbols for the atomic weights of the elements hydrogen and oxygen.	1. H_2O is the *formula for the molecule* of water with H as the symbol for the atom of hydrogen and O as the symbol for the atom of oxygen.
2. H_2SO_4 is the *formula for the molecular weight* of hydrogen sulfate with H and S and O as symbols for the atomic weights of the elements hydrogen, sulfur, and oxygen.	2. H_2SO_4 is the *formula for the molecule* of hydrogen sulfate with H and S and O as symbols for the atoms of hydrogen, sulfur, and oxygen.

Thus it is that the formula for the molecular weight of a substance and for the molecule of said substance look alike in every detail; the difference lies in the mind and what the user of the formula wants it to tell at the time.

Formulas for more complex compounds. It stands to reason, that the more complex the composition of the molecular weight of a substance, the more complex must be its molecule; hence it follows that the formula representation for the composition of said molecular weight and said molecule must be correspondingly complex.

The formulas thus far presented, such as those listed in A in the accompanying tabulation, have been in respect to less complex substances; but formulas that represent more complex substances are given in B. These apply to compounds which contain more than one of such two-or-more-element radical constituents (p. 130) as the hydroxyl radical, the sulfate radical, and the nitrate radical.

A

Formulas for less complex substances

For molecular weights		*For molecules*
Oxygen (substance)	O_2	O_2
Hydrogen chloride	HCl	HCl
Water	H_2O	H_2O
Hydrogen sulfate	H_2SO_4	H_2SO_4

B

Formulas for more complex substances

For molecular weights		*For molecules*
Magnesium hydroxide	$Mg(OH)_2$	$Mg(OH)_2$
Ferric sulfate	$Fe_2(SO_4)_3$	$Fe_2(SO_4)_3$
Calcium nitrate	$Ca(NO_3)_2$	$Ca(NO_3)_2$

In these instances the shorthand expression for the composition of the radical is enclosed in parenthesis and the number of radical weights that are present within the molecular weight, or of atom groups within the molecule, is indicated as represented in the formulas given above. And here is an example with more detail:

$Mg(OH)_2$ for the *molecular weight* means that one molecular weight of magnesium hydroxide is composed of 1 atomic weight of magnesium and 2 hydroxyl radical weights, each radical weight being composed of —

1 atomic weight of oxygen and
1 atomic weight of hydrogen.

$Mg(OH)_2$ for the *molecule* means that one molecule of magnesium hydroxide is composed of 1 atom of magnesium and 2 hydroxyl atom groups, each atom group being composed of —

1 atom of oxygen and
1 atom of hydrogen.

More will be said concerning radical parts of compounds later (p. 130).

Making the formula "talk." Now that the main items concerning the significance of the formula have been presented let us proceed to make formulas work for us. During this procedure much of the foregoing study will pass in review and another item or two will be introduced.

When is the formula for a substance used correctly? Certainly *not* as an abbreviation for the name of a substance if the formula is to have the quantitative significance of its intent! Indeed, if it is to carry this significance the formula should be used only under such circumstances as the following:

In terms of measurable quantities to represent:

1. The molecular weight of the substance in the abstract.
2. The gram molecular weight of the substance, or the molecular weight in weight units other than grams.

Theoretically, 3. The formula is used correctly to represent the molecule of a substance.

For example. The formula $KClO_3$ for potassium chlorate is used correctly: *from a large quantity viewpoint,*

1. to represent 122.553 parts by weight of potassium chlorate.
2. or to represent 122.553 grams of this compound.

Theoretically, 3. this formula $KClO_3$ is used correctly to represent one molecule of potassium chlorate.

Computed data

$$\underbrace{\underset{39.096}{K} \quad \underset{35.457}{Cl} \quad \underset{3 \times 16}{O}}_{122.553}$$

(Molecular weight)

The formula an aid in computing the molecular weight of a substance. With the formula given for the molecular weight of

a substance, the atomic weights (see table) can be introduced in respect to the symbols which represent them and the molecular weight for the substance computed. Here is an example:

Formula for potassium phosphate.	K_3	P	O_4
Introducing atomic weights.	$\underbrace{3 \times \underline{39.096}}$	$\underbrace{1 \times \underline{30.98}}$	$\underbrace{4 \times \underline{16}}$
Total elements within molecular weight.	117.288	30.98	64
Molecular weight for potassium phosphate.		$\underline{212.268}$	

How is the formula interpreted? This must depend upon whether the formula is to be interpreted in reference to the composition of a measurable quantity of the substance: namely, its molecular weight; or in reference to the composition of its believed-in molecule. Thus:

Example one. Given the formula Na_2SO_4 for sodium sulfate:

As the formula stands, in reference to the molecular weight, it tells that one molecular weight of sodium sulfate is composed of 2 atomic weights of sodium, 1 atomic weight of sulfur and 4 atomic weights of oxygen.

But with quantitative data obtained, still as to the molecular weight, this formula tells that 142.054 parts by weight of sodium sulfate is composed of 2 × 22.997 parts by weight of sodium, 1 × 32.06 parts by weight of sulfur, and 4 × 16 parts by weight of oxygen.

Computed data

$$\underbrace{\begin{array}{ccc} Na_2 & S & O_4 \\ 2 \times \underline{22.997} & \underline{32.06} & 4 \times \underline{16} \end{array}}_{\underline{142.054}}$$

Or in grams, the formula tells that 142.054 grams of sodium sulfate is composed of 2 × 22.997 grams of sodium, 1 × 32.06 grams of sulfur, and 4 × 16 grams of oxygen.

Theoretically, this formula, Na_2SO_4, tells that one molecule of sodium sulfate is composed of 2 atoms of sodium, 1 atom of sulfur, and 4 atoms of oxygen.

Example two. Given the more complex formula $Al_2(CO_3)_3$:

As the formula stands, in reference to the molecular weight, it tells that one molecular weight of aluminium carbonate is composed of 2 atomic weights of aluminium and 3 carbonate radical weights, each radical weight being composed of 1 atomic weight of carbon and 3 atomic weights of oxygen.

But with quantitative data obtained, still as to the molecular weight, this formula tells that 233.97 parts by weight of aluminium carbonate is composed of 2 × 26.97 parts by weight of aluminium and 3 × 60.01 parts by weight of carbonate, each carbonate being composed of 1 × 12.01 parts by weight of carbon and 3 × 16 parts by weight of oxygen.

Computed data

$$\underbrace{\begin{array}{c} Al_2 \\ 2 \times \underline{26.97} \end{array} \underbrace{\left(\begin{array}{cc} C & O_3 \\ \underline{12.01} & \underbrace{3 \times \underline{16}}_{48} \end{array} \right)_3}_{3 \times \underline{60.01}}}_{\underline{233.97}}$$

Theoretically, this formula tells that one molecule of aluminium carbonate is composed of 2 atoms of aluminium and 3 carbonate *atom groups,* each being composed of 1 atom of carbon and 3 atoms of oxygen.

Formulas for simple substances. Formulas for the simple substances as listed below tell their own story. Six simple substances with which we shall be dealing — bromine, chlorine, hydrogen, iodine, nitrogen, and oxygen — have two atomic weights of the elements combined within their molecular weights; hence their molecules are believed to contain two atoms each. And formulas for their molecular weights and molecules are written accordingly. The substance phosphorus has four atomic weights of the element within its molecular weight, while its molecule is believed to contain four atoms; and the formula tells this tale.

Substance	*Molecular weight*	*Symbol for molecular weight*	*Symbol for molecule*
Bromine	159.832	Br_2	Br_2
Chlorine	70.914	Cl_2	Cl_2
Hydrogen	2.016	H_2	H_2
Iodine	253.84	I_2	I_2
Nitrogen	28.016	N_2	N_2
Oxygen	32.	O_2	O_2
Phosphorus	123.92	P_4	P_4
Aluminium	26.97	Al	Al
Barium	137.36	Ba	Ba
Calcium	40.08	Ca	Ca
Carbon	12.01	C	C
Copper	63.57	Cu	Cu
Iron	55.85	Fe	Fe
Lead	207.21	Pb	Pb
Magnesium	24.32	Mg	Mg
Mercury	200.61	Hg	Hg
Potassium	39.096	K	K
Silver	107.88	Ag	Ag
Sulfur	32.06	S	S
Zinc	65.38	Zn	Zn

But for reasons that we shall not enter into, the molecular weights of other simple substances have been difficult to obtain correctly. Therefore the molecular weights of such of these simple substances as we shall encounter are ***regarded*** as containing only one atomic weight, each, of the elements respectively concerned; hence, theoretically, the molecule of each of these simple substances is ***regarded*** as being composed of only one atom. This is indicated in the formulas as given in the accompanying table, the subscript *one* being usually omitted.

It should be a comparatively easy task for the student to fix in mind the formulas for the first seven of the simple substances listed and then to remember, by process of elimination, what formulas for other simple substances should be. This information readily at hand will be of considerable service as our study proceeds. The following is an interpretation of a representative formula for a simple substance:

The formula H_2 for the *molecular weight of hydrogen:*

1. As the formula stands it tells, in general, that *one molecular weight* of hydrogen substance is composed of two atomic weights of hydrogen element.

2. With atomic weights substituted for the symbols for which they stand and the molecular weight calculated, this formula tells, in general, that 2.016 parts by weight of hydrogen substance is composed of 2×1.008 parts by weight of hydrogen element.

$$\underbrace{\overset{H_2}{2 \times 1.008}}_{2.016}$$

3. *Theoretically,* H_2 tells that *one molecule* of hydrogen substance is believed to be composed of two atoms of hydrogen element.

SHORTHAND AS TO CHEMICAL REACTIONS

Formula equation for molecular weight involvement. Once formulas for molecular weights of substances are obtained, the possibility of representing in shorthand manner the quantities of substances mutually participating in a reaction becomes immediately possible; and the label that has come to be applied to the shorthand assemblage that results is the *chemical equation,* or more frequently called just *the equation for the reaction.* The following are reasonings in the light of definite examples as to why such a shorthand device is possible (see accompanying list of formulas for molecular weights of participating substances):

The substance	*Formula for molecular weight*	*Formula for molecule*
Carbon dioxide......	CO_2	CO_2
Hydrogen...........	H_2	H_2
Glucose.............	$C_6H_{12}O_6$	$C_6H_{12}O_6$
Oxygen.............	O_2	O_2
Methane............	CH_4	CH_4
Methyl alcohol......	CH_3OH	CH_3OH
Water..............	H_2O	H_2O

Example one.

Water decomposes to make the substances hydrogen and oxygen in 2 to 2 to 1 multiples, respectively, as to their molecular weights:

Water ⟶	Hydrogen	+ Oxygen
2	2	1
Molecular weights	Molecular weights	Molecular weight

Therefore, it is possible to represent these quantities in shorthand manner through the same multiples as to the *formulas for the molecular weights* of these substances:

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

Example two.

Ethylene reacts with oxygen to make water and carbon dioxide in 1 to 3 to 2 to 2 multiples, respectively, as to their molecular weights:

Ethylene +	Oxygen ⟶	Water +	Carbon dioxide
1	3	2	2
Molecular weight	Molecular weights	Molecular weights	Molecular weights

Therefore, it is possible to represent these quantities of these substances as involved in this reaction through the same multiples as to the *formulas for their molecular weights:*

$$C_2H_4 + 3\,O_2 \longrightarrow 2\,H_2O + 2\,CO_2$$

Related equation for ultimate molecule line-up. Since formulas for molecular weights of substances and formulas for molecules of substances look alike (see listing of formulas, p. 123), and since the known number of molecular weights of substances that participate in the large quantity reaction and the believed-in number of molecules that engage in the ultimate unit reaction are the same, it becomes apparent that: (1) the equation for the large quantity reaction in which *molecular weights* of substances are their measuring units, and (2) the equation for the *molecule involvement* in said reaction must look alike, although they tell entirely different stories to those who understand this relationship. Thus:

	Ethylene + Oxygen ⟶ Water + Carbon dioxide
In large quantity reaction, *formulas are for molecular weights*	$C_2H_4 + 3\,O_2 \longrightarrow 2\,H_2O + 2\,CO_2$
In ultimate reaction, *formulas are for molecules*	$C_2H_4 + 3\,O_2 \longrightarrow 2\,H_2O + 2\,CO_2$

The equation interpreted. Now that the equation has been presented it would be well to take an equation and let it tell the quantitative story of its intent. For this purpose let us turn to the equation for the reaction between methyl alcohol and oxygen:

Methyl alcohol + Oxygen ⟶ Water + Carbon dioxide

$$2\,CH_3OH + 3\,O_2 \longrightarrow 4\,H_2O + 2\,CO_2$$

(1) *As the equation stands,* with molecular weights as units for substances: this equation tells that 2 molecular weights of methyl alcohol react with 3 molecular weights of oxygen to make 4 molecular weights of water and 2 molecular weights of carbon dioxide.

(2) But *with numerical values for* molecular weights computed:

$$2\ \underbrace{\begin{matrix}CH_3OH\\ 1\times 12.01\\ 3\times 1.008\\ 1\times 16\\ 1\times 1.008\end{matrix}}_{\underline{32.042}} \quad + \quad 3\ \underbrace{\begin{matrix}O_2\\ 2\times 16\end{matrix}}_{\underline{32}} \longrightarrow 4\ \underbrace{\begin{matrix}H_2O\\ 2\times 1.008\\ 1\times 16\end{matrix}}_{\underline{18.016}} \quad + \quad 2\ \underbrace{\begin{matrix}CO_2\\ 1\times 12.01\\ 2\times 16\end{matrix}}_{44.01}$$

In general, this equation tells that 2 × 32.042 parts by weight of methyl alcohol react with 3 × 32 parts by weight of oxygen to make 4 × 18.016 parts by weight of water and 2 × 44.01 parts by weight of carbon dioxide.

(3) Or *in actual quantities, in grams,* this equation tells that 2 × 32.042 grams of methyl alcohol react with 3 × 32 grams of oxygen to make 4 × 18.016 grams of water and 2 × 44.01 grams of carbon dioxide.

(4) *Theoretically,* this equation tells that 2 molecules of methyl alcohol react with 3 molecules of oxygen to make 4 molecules of water and 2 molecules of carbon dioxide.

The equation provides evidence of chemical equalities. ***First, in relation to the law of chemical change*** the equation provides evidence that:

$$\left.\begin{array}{l}\text{the quantities of } \textit{elements}\\ \text{that are present within}\\ \text{substances before the reaction}\end{array}\right\}\begin{array}{c}\text{are}\\ \text{equal}\\ \text{to}\end{array}\left\{\begin{array}{l}\text{the quantities of } \textit{elements}\\ \text{that are present within the}\\ \text{substances that are made.}\end{array}\right.$$

By way of an example, let us turn to the equation for the reaction that takes place between glucose and oxygen, remembering that *elements are measured by their atomic weights* and that there are as many atomic weights of the elements as there are symbol multiples:

$$\begin{array}{ccccccc}\text{Glucose} & + & \text{Oxygen} & \longrightarrow & \text{Water} & + & \text{Carbon dioxide}\\ C_6H_{12}O_6 & + & 6\ O_2 & \longrightarrow & 6\ H_2O & + & 6\ CO_2\end{array}$$

Elements within substances before the reaction:	*Elements within substances after the reaction:*
6 atomic weights of carbon in glucose	6 atomic weights of carbon in carbon dioxide
12 atomic weights of hydrogen in glucose	12 atomic weights of hydrogen in water
18 atomic weights of oxygen distributed in glucose and oxygen	18 atomic weights of oxygen distributed in water and carbon dioxide

Second, the chemical equation provides evidence as to the law of conservation of mass: namely,

$$\left.\begin{array}{l}\text{the inclusive weight}\\ \text{of } \textit{substances} \text{ that exist}\\ \text{before a reaction}\end{array}\right\}\text{is equal to}\left\{\begin{array}{l}\text{the inclusive weight of}\\ \textit{substances} \text{ that are made}\\ \text{(p. 18).}\end{array}\right.$$

As an example let us take the above equation, but this time remembering that *the measuring units for substances are their molecular weights:*

$$\begin{array}{ccccccc}\text{Glucose} & + & \text{Oxygen} & \longrightarrow & \text{Water} & + & \text{Carbon dioxide}\\ C_6H_{12}O_6 & + & 6\ O_2 & \longrightarrow & 6\ H_2O & + & 6\ CO_2\\ \underbrace{\begin{array}{c}6 \times 12.01\\ 12 \times 1.008\\ 6 \times 16\end{array}}_{\underline{180.156}} & & \underbrace{2 \times 16}_{\underline{32}} & & \underbrace{\begin{array}{c}2 \times 1.008\\ 1 \times 16\end{array}}_{\underline{18.016}} & & \underbrace{\begin{array}{c}1 \times 12.01\\ 2 \times 16\end{array}}_{\underline{44.01}}\end{array}$$

Substances before the reaction:		*Substances after the reaction:*	
Glucose 1 × 180.156 =	180.156	Water 6 × 18.016 =	108.096
Oxygen 6 × 32 =	192	Carbon dioxide 6 × 44.10 =	264.06
Inclusive weight of these substances	372.156	Inclusive weight of these substances	372.156

Assembling equations. So it is that the equation is one of the fundamentally important measuring tools of the chemist. Consequently, knowing what equations are about, how to interpret them, and how to assemble them should become part of the equipment of every serious student of chemistry. Already the interpretation of an equation has been presented but not the manner of obtaining an equation. Therefore let us now assemble the equation for the reaction between iron and oxygen by way of an introduction to the working scheme involved.

The ***first step*** is to know what substances participate in the reaction, and the word equation serves as such a handy record. ***Second,*** one should set down the ***correct*** formulas for these substances; furthermore, correct formulas should never be altered. As to the reaction suggested, then, these two steps are as follows:

$$\text{Iron} + \text{Oxygen} \longrightarrow \text{Ferric oxide (Iron rust)}$$
$$?\,Fe + \;?\,O_2 \longrightarrow \;?\,Fe_2O_3$$

Third, as an aid in arriving at the formula multiples, one should bear in mind that they must be such that the number of atomic weights of iron and oxygen elements within the iron and oxygen substances before the reaction will all be found present within the ferric oxide made.

So, as to oxygen element, inspection shows that it is combined 2 atomic weights at a time in 1 molecular weight of oxygen substance, whereas in ferric oxide it is combined in 3 atomic weights at a time; hence, 6 atomic weights of oxygen must be provided. This calls for 3 molecular weights of oxygen substance before the reaction and 2 molecular weights of ferric oxide made:

$$?\,Fe + 3\,O_2 \longrightarrow 2\,Fe_2O_3$$

But these two molecular weights of ferric oxide product contain a total of 4 atomic weights of iron element which must be provided in 4 molecular weights of the beginning iron substance. Thus the complete equation for this reaction is as follows:

$$4\,Fe + 3\,O_2 \longrightarrow 2\,Fe_2O_3$$

In general, then, the steps in assembling a chemical equation are: ***First.*** One must know *what substances are involved before and*

after the reaction. For the beginning student it would be well to assemble this information through the medium of the *word equation.*

Second. One should set down the *correct formulas* for the molecular weights of the substances.

Third. Keeping in mind the law of chemical change one must then, by inspection, arrive eventually at such *whole number formula multiples* as will provide for equal numbers of symbol weights of elements within said formulas before and after the reaction thus represented.

FORMULAS AND EQUATIONS USED TOWARD PRACTICAL ENDS

The formula put to work. The formula for any compound is of practical value because it tells of the weight relationship that must always exist: (1) between the constituent elements as to each other, and (2) between the constituent elements and the compound as a whole. For example:

1. Suppose the problem is that of ascertaining the quantity of oxygen element that must be present in 15 ounces of potassium chlorate, then:

$$\underset{\substack{\text{ounces}\\\text{of oxygen}}}{x} : \underset{\substack{\text{ounces}\\\text{of potassium}\\\text{chlorate}}}{15} = 48 : 122.553$$

$$\underbrace{\overbrace{\begin{matrix} & & ? \\ K & Cl & O_3 \\ \underline{39.096} & \underline{35.457} & \underbrace{3\times \underline{16}}_{48}\end{matrix}}^{15\text{ ounces}}}_{122.553}$$

$$x = \frac{15 \times 48}{122.563} = 5.87 \text{ ounces of oxygen combined in 15 ounces of potassium chlorate.}$$

2. Or the problem might be as to what quantity of sodium sulfate must be weighed out to contain 3 pounds of the element sodium, in which case:

$$\underset{\substack{\text{pounds}\\\text{of sodium}}}{3} : \underset{\substack{\text{pounds}\\\text{of sodium}\\\text{sulfate}}}{x} = 45.994 : 142.054$$

$$\underbrace{\overbrace{\begin{matrix} \text{3 pounds} & & \\ Na_2 & S & O_4 \\ \underbrace{2\times \underline{22.997}}_{45.994} & \underline{32.06} & 4\times \underline{16}\end{matrix}}^{?}}_{142.054}$$

$$x = \frac{3 \times 142.054}{45.994} = 9.26 \text{ pounds of sodium sulfate necessary to contain 2 pounds of sodium.}$$

The equation put to work. The equation for any specific reaction makes it possible to obtain information concerning the *weight relationship that must always exist between participating substances.* For example:

Suppose the problem is: how much oxygen is necessary to react with 10 ounces of methane?

The first step must be to obtain the *correct* equation for the reaction, then the molecular weights of these two substances through their formulas. Thus:

$$\begin{array}{ccccccc} \text{Methane} & + & \text{Oxygen} & \longrightarrow & \text{Water} & + & \text{Carbon dioxide} \\ \text{10 ounces} & & ? & & & & \end{array}$$

$$\overbrace{\underset{\underbrace{\begin{array}{c}1\times 12.01\\ 4\times 1.008\end{array}}_{\underline{16.042}}}{CH_4}} + 2\ \overbrace{\underset{\underbrace{2\times 16}_{\underline{32}}}{O_2}} \longrightarrow 2\,H_2O + CO_2$$

Therefore $\underset{\substack{\text{ounces}\\ \text{of methane}}}{10} : \underset{\substack{\text{ounces}\\ \text{of oxygen}}}{x} = 16.042 : 64$

$x = \dfrac{10 \times 64}{16.042} = 39.9$ ounces of oxygen necessary to react with 10 ounces of methane.

Obviously, the possibility of putting the formula for a compound and the equation for a chemical reaction to work in such practical ways as presented in the foregoing discussion have almost inconceivable significance. Not only chemists but also manufacturers are interested in making use of these handy quantitative tools, since:

Through the aid of the *formula* the chemist or the manufacturer is able to compute:

1. The *quantity of any element* of his need which must be present in a given quantity of a compound containing it.

2. The *quantities of the elements* concerned which must be obtained for the making of a given weight of a desired compound.

Through the aid of the *equation* the chemist or the manufacturer is able to compute:

1. The *quantity of any substance* which must be obtained before the reaction in order to make a desired quantity of a desired substance as product.

2. The *quantities of substances* that will be made from given quantities of substances entering into the reactions concerned.

And the formulas for molecular weights of compounds, the equations for chemical reactions, once *correctly* obtained, provide the means whereby answers to such important questions as these become possible.

Questions

Note. — In connection with this study refer to the table of atomic weights on the back cover of this text whenever necessary.

1. From two viewpoints, what does a chemical symbol represent? Illustrate in reference to: N for nitrogen, Ag for silver, C for carbon, and I for iodine.

2. From two different viewpoints what, in general, does a chemical formula represent? Give three instances in which a formula may be used correctly. Illustrate by reference to the formula CO_2.

3. Assemble in good form the quantitative data provided by each of the following formulas and compute the molecular weight for each substance:

$$AgNO_3,\quad Ca(OH)_2,\quad H_3PO_4,\quad Fe_2(CO_3)_3$$

4. Making use of the quantitative data obtained in question 3, interpret each of the above formulas: (a) in general terms, (b) in gram terms. Also interpret each of these formulas from the standpoint of the molecule.

5. What quantitative information (from two viewpoints) concerning the simple substances represented is provided by each of the following formulas:

$$O_2,\quad Pb,\quad Br_2,\quad P_4$$

6. Interpret each of the following equations (a) with formulas representing molecular weights of substances; (b) with formulas representing molecules of said substances:

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$$
$$P_4 + 5\,O_2 \longrightarrow 2\,P_2O_5$$
$$2\,NaCl + H_2SO_4 \longrightarrow 2\,HCl + Na_2SO_4$$

7. In respect to each equation in question 6, compute the molecular weights of the substances involved and interpret the equation: (a) in gram terms; (b) in general terms.

8. Assemble word and formula equations for the reaction that results from each of the following contacts (select the necessary formulas from the accompanying list):

a. The decomposition of water.
b. Reaction of copper and silver nitrate.
c. Reaction of potassium iodide and lead nitrate.
d. Rusting of iron.

Formula list

Ag	$AgNO_3$
Cu	$Cu(NO_3)_2$
Fe	Fe_2O_3
H_2	H_2O
O_2	KI
PbI_2	KNO_3
	$Pb(NO_3)_2$

9. What weight of potassium chlorate (formula $KClO_3$) would contain 10 ounces of oxygen element?

10. How much carbon element is contained within 1 gram of glucose (formula $C_6H_{12}O_6$)? How much oxygen? How much hydrogen?

11. How much oxygen must be brought to the cells to react with 1 gram of glucose? How much carbon dioxide is made from the reaction? How much water? Formula equation for this reaction is as follows:

$$C_6H_{12}O_6 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O$$

12. (a) In the making of cakes and biscuits what *relative* weights of sodium bicarbonate and cream of tartar must be mixed for exact reaction with no excess of either remaining? (b) What *relative* weight of Rochelle salt will be left in the cake? (c) If *two grams* of sodium bicarbonate are measured out, how much cream of tartar must be used and how much Rochelle salt will be left in the cake?

$$\underset{\text{Sodium bicarbonate}}{NaHCO_3} + \underset{\text{Cream of tartar}}{KHC_4H_4O_6} \longrightarrow H_2O + CO_2 + \underset{\text{Rochelle salt}}{KNaC_4H_4O_6}$$

13. In respect to the reaction between methane and oxygen (p. 128), how does the equation provide evidence as to:

a. The law of chemical change?
b. The law of conservation of mass?

CHAPTER XI

Something Concerning Bases, Acids, and Salts. Radicals

They are composed of radical parts. Every acid, base, and salt is composed of two more or less loosely combined parts called radicals. Some radicals, such as chloride, are composed of but one element each; others, such as nitrate, are composed of two (or more) closely combined elements.

When any pair of these compounds, such as an acid and a base or a base and a salt, are in contact with each other *in water solution*, an interchange of their partner radicals begins at once to take place in a double decomposition reaction, as the result of which two new compounds, but including these same radicals, are made. For example:

When hydrochloric acid and sodium nitrate are the compounds in contact with each other in water solution an immediate interchange of their partner parts sets in and the two new compounds made are nitric acid and sodium chloride:

Hydrogen chloride + Sodium nitrate ⇄ Hydrogen nitrate + Sodium chloride

$$HCl + NaNO_3 \rightleftharpoons HNO_3 + NaCl$$

And contrariwise when hydrogen nitrate and sodium chloride get into contact the reverse reaction sets in whereby sodium nitrate and nitric acid are made.

Formulas for a few of the hundreds of compounds known that are composed of these easily interchangeable, loosely combined radical parts are as follows; the dot, although not usually indicated, is introduced here in order to set off the radical parts of each compound and to indicate, at the same time, the point of loose combination:

Hydrogen chloride		*Sodium nitrate*	
H ·	Cl	Na ·	NO_3
hydrogen radical	chloride radical	sodium radical	nitrate radical
Hydrogen nitrate		*Sodium chloride*	
H ·	NO_3	Na ·	Cl
hydrogen radical	nitrate radical	sodium radical	chloride radical

Hydrogen sulfate		*Potassium hydroxide*	
H_2 ·	SO_4	K ·	OH
hydrogen radical	sulfate radical	potassium radical	hydroxide radical

Radicals that are peculiar to all bases, to all acids, and to all salts, respectively, will be considered presently as we begin preliminary studies of these important classes of compounds.

Theoretical explanation. For the theoretical explanation of these easily displaced radical parts of compounds one must turn to their molecules in which it is assumed that the single atoms or atom groups, which comprise the radical parts of molecules, are in loose combination with each other, hence are ready to be displaced easily by other selected atoms or atom groups. Thus:

Representing specific molecules with dot indicating point of loose combination

Hydrogen chloride

$H \cdot Cl$

Sodium nitrate

$Na \cdot ON^{O}_{O}$

Hydrogen nitrate

$H \cdot ON^{O}_{O}$

Sodium chloride

$Na \cdot Cl$

Hydrogen sulfate

$\begin{matrix}H\\H\end{matrix} \cdot \begin{matrix}O_{S}O\\O^{S}O\end{matrix}$

Potassium hydroxide

$K \cdot OH$

BASES

Constituent radicals. The radicals which enter into the composition of every base are as follows:

A metal radical which is composed of a more or less easily displaced metal element, or	and	***The hydroxyl radical*** which is composed of hydrogen and oxygen in close combination.

A metal-acting radical which is composed of a specific selection of two or more nonmetal elements in close combination with each other. These radicals are "metal-acting" because they contribute to compounds similar to those in which metal radicals are found. Examples are:

Ammonium radical	(NH_4)
Methyl radical	(CH_3)
Ethyl radical	(C_2H_5)
Glyceryl radical	(C_3H_5)

The radical common to bases. The radical which is common to all bases is the *hydroxyl radical,* while the variable and that which determines the specific base, is the *metal* or *metal-acting radical.*

Outstanding bases. Some bases of more or less frequent occurrence are listed in the table given below; chemist's names for them and common names, if any, are given, also formulas for their molecular weights and molecules.

Chemist's name	*Common name*	*Component of*	*Formula for molecular weight and molecule*
Inorganic bases			
Sodium hydroxide	Caustic soda		$NaOH$
Potassium hydroxide	Caustic potash		KOH
Calcium hydroxide	Slaked lime	Limewater Milk of lime	$Ca(OH)_2$
Magnesium hydroxide		Milk of magnesia	$Mg(OH)_2$
Ammonium hydroxide	Aqua ammonia Spirits of hartshorn	Household ammonia	NH_4OH
Organic Bases or Alcohols			
Methyl hydroxide, or Methyl alcohol, or Methanol	Wood alcohol		CH_3OH
Ethyl hydroxide, or Ethyl alcohol, or Ethanol	Grain alcohol or Alcohol spirits	Fermenting fruits and grains	C_2H_5OH
Glyceryl hydroxide, or Glyceryl alcohol, or Glycerol	Glycerine		$C_3H_5(OH)_3$

Inorganic and organic bases. It should be noted that although most *inorganic bases* contain a real metal radical there is one such base, ammonium hydroxide, that contains a metal-acting radical. It should also be observed that the metal-acting radicals within *organic bases,* or *alcohols,* are composed of the two elements carbon and hydrogen. There are many chemists who do not include alcohols among bases. But the fact remains that in certain important respects, as we shall see later, alcohols do react like bases; it is for this reason that they are included here.

In reaction with red litmus. When bases are in water solution they have a marked tendency to react with selected colored sub-

stances in characteristic manner. One such colored compound is *red litmus* and the product made from its reaction with bases is *blue litmus*. Two of these reactions are represented by word equations as follows:

In water solution

$$\left.\begin{array}{l}\text{Sodium hydroxide} + \text{Red litmus} \longrightarrow \text{Blue litmus} \\ \text{Ammonium hydroxide} + \text{Red litmus} \longrightarrow \text{Blue litmus}\end{array}\right\} \begin{array}{l}\text{in conspicuous} \\ \text{quantities}\end{array}$$

A caution. Because of the conspicuous reaction with red litmus on the part of some frequently occurring bases, many students are led into believing that red litmus can be used as an infallible test for the presence of a base. But this belief is in error since there are some compounds which, although they are bases and have a tendency to react thus with red litmus, are not able for one reason or another to carry the reaction far enough to make conspicuous quantities of the blue litmus product. Accordingly:

$$\left.\begin{array}{l}\text{Copper hydroxide} + \text{Red litmus} \rightarrow \text{Blue litmus} \\ \quad\text{(only slightly soluble)} \\ \text{Any alcohol} + \text{Red litmus} \longrightarrow \text{Blue litmus} \\ \quad\text{(a \textit{very} poor base)}\end{array}\right\} \begin{array}{l}\text{in such negligible} \\ \text{quantities as not} \\ \text{to become evident.}\end{array}$$

ACIDS

Constituent radicals. The radical parts which enter into the composition of every acid are as follows:

A hydrogen radical which is composed of easily displaced hydrogen element.

and

A radical, called ***an acid radical,*** which is composed of:

1. A *nonmetal element,* such as chlorine, bromine, iodine, or sulfur. When such an element does comprise the entire acid radical, said radical is called:
   chlor*ide* radical Cl
   brom*ide* radical . . . . Br
   iod*ide* radical I
   sulf*ide* radical . . . . S

2. A *nonmetal element and oxygen,* such as,
   nitr*ate* . . . . . (NO_3) nitr*ite* . . . . . (NO_2)
   chlor*ate* . . . (ClO_3) chlor*ite* . . . . (ClO_2)
   sulf*ate* . . . . . (SO_4) sulf*ite* . . . . . (SO_3)
   phosph*ate* . (PO_4) phosph*ite* . . (PO_3)

3. *Carbon, hydrogen, and oxygen,* as in the
   acet*ate* radical . . . . ($C_2H_3O_2$)
   tartr*ate* radical . . . . ($C_4H_4O_6$)
   stear*ate* radical . . . . ($C_{17}H_{35}CO_2$)

And any compound which is composed of a hydrogen radical and any one of the many so-called acid radicals is an acid.

The common radical. Obviously the radical that is common to all acids is the *hydrogen radical,* while the variable, consequently that which determines the specific acid, is the acid radical.

Representative acids and naming scheme. Representative acids are listed in the table below together with the *two names* which are applied to them: *one name* mentions the presence of both the hydrogen radical and the acid radical but does not specify that the compound is an acid; the *second name* does not mention both of the radicals present but does tell that the compound is an acid.

Furthermore, upon making a study of the naming of the following acids it should be noted that there is a definite naming scheme, involving suffixes and in some instances prefixes, which has a bearing on their composition: as to (1) whether the acids do or do not contain oxygen, (2) the relative proportions of oxygen in acids containing the same nonmetal element.

Names for acids which specify by name the **two radicals** *present*	*Names which do* **not** *name the radicals but tell that compounds are acids*	*Formula for molecular weight and molecule*
1. Acids that do not contain oxygen		
Hydrogen chlor*ide*.........	*Hydro* chlor*ic acid*........	$H\ Cl$
Hydrogen brom*ide*........	*Hydro* brom*ic acid*	$H\ Br$
Hydrogen sulf*ide*..........	*Hydro* sulfur*ic acid*.......	H_2S
2. Usually occurring acids that do contain oxygen		
Hydrogen nitr*ate*..........	Nitr*ic acid*...............	$H\ NO_3$
Hydrogen chlor*ate*.........	Chlor*ic acid*..............	$H\ ClO_3$
Hydrogen brom*ate*.........	Brom*ic acid*..............	$H\ BrO_3$
Hydrogen sulf*ate*..........	Sulfur*ic acid*.............	$H_2\ SO_4$
Hydrogen carbon*ate*.......	Carbon*ic acid*............	$H_2\ CO_3$
Hydrogen phosph*ate*.......	Phosphor*ic acid*...........	$H_3\ PO_4$
3. Acids that contain a less proportion of oxygen		
Hydrogen nitr*ite*..........	Nitr*ous acid*.............	$H\ NO_2$
Hydrogen chlor*ite*.........	Chlor*ous acid*............	$H\ ClO_2$
Hydrogen brom*ite*.........	Brom*ous acid*............	$H\ BrO_2$
Hydrogen sulf*ite*..........	Sulfur*ous acid*...........	$H_2\ SO_3$
Hydrogen phosph*ite*.......	Phosphor*ous acid*.........	$H_3\ PO_3$
4. Acids that contain a still less proportion of oxygen		
Hydrogen *hypo* chlor*ite*.....	*Hypo* chlor*ous acid*........	$H\ ClO$
Hydrogen *hypo* brom*ite*....	*Hypo* brom*ous acid*........	$H\ BrO$

5. Acids that contain a higher proportion of oxygen than in corresponding *ate* or *ic* acid

Hydrogen *per* chlor*ate*......	*Per* chlor*ic acid*...........	$H\ ClO_4$
Hydrogen *per* iod*ate*......	*Per* iod*ic acid*.	$H\ IO_4$

6. Names of organic acids

Hydrogen acet*ate*..........	Acet*ic acid*...............	$H\ C_2H_3O_2$
Hydrogen tartr*ate*.........	Tartar*ic acid*.............	$H_2\ C_4H_4O_6$
Hydrogen palmit*ate*........	Palmit*ic acid*.............	$H\ C_{15}H_{31}CO_2$
Hydrogen stear*ate*...	Stear*ic acid*..............	$H\ C_{17}H_{35}CO_2$
Hydrogen ole*ate*...........	Ole*ic acid*................	$H\ C_{17}H_{33}CO_2$

So it is that, in general, the naming scheme for acids is as follows; the dash indicates the naming position for the particular nonmetal involved:

	One name	The other name
If an acid does not contain oxygen	Hydrogen—ide....................	Hydro—ic acid

	One name	The other name
If the acid does contain oxygen	Hydrogen—ate....................	——ic acid
	Hydrogen—ite....................	——ous acid
	Hydrogen hypo—ite................	Hypo—ous acid
	Hydrogen per —ate................	Per——ic acid

In reaction with blue litmus. When acids are in water solution they exhibit a marked tendency, as do bases, to react with selected colored substances to make substances of a different color. One such substance is *blue litmus* with which acids, in water solution, have a tendency to make *red litmus*. This it will be noted is the reverse of the effect produced by bases (p. 133). Here are some specific examples:

In water solution

$$\left.\begin{array}{l}\text{Hydrochloric acid} + \text{Blue litmus} \longrightarrow \text{Red litmus}\\ \text{Sulfuric acid} + \text{Blue litmus} \longrightarrow \text{Red litmus}\\ \text{Acetic acid} + \text{Blue litmus} \longrightarrow \text{Red litmus}\end{array}\right\}\text{in conspicuous quantities}$$

A caution. And again, as with bases, this common and conspicuous response as to many acids in reaction with blue litmus has given rise to the misunderstanding that it can be used as an infallible test for the presence of all acids. This is not the case, since there are compounds which, although acids, are such poor ones that they do not react with blue litmus in sufficient quantities to make visible amounts of red litmus.

SALTS

Constituent radicals. Radicals that contribute to every salt are as follows:

A metal radical and *An acid radical*
or
A metal-acting radical

It is because salts are composed of metal or metal-acting radicals and acid radicals that many of them can be made readily from reactions between bases, which provide the desired metal radicals, and acids, which provide the acid radicals (p. 133). For example:

Sodium sulfate can be made from the reaction of *sodium* hydroxide, which provides the sodium radical, with sulfuric acid, which provides the *sulfate* radical. This reaction is represented as follows:

$$\text{Base} + \text{Acid} \longrightarrow \text{Salt} + \text{Water}$$
$$2\,NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,H_2O$$

Nomenclature. The chemist's method for naming salts is very simple indeed. It consists merely of specifying the two radicals that are present, the acid radicals carrying the same names as they do when they contribute to acids. Consequently, from a naming angle salts are:

	Examples	*Formulas*
Metal (or metal-acting).......*ides*	Sodium chloride	$Na\ Cl$
	Ammonium chloride	NH_4Cl
Metal (or metal-acting)......*ates*	Sodium chlorate	$Na\ ClO_3$
	Ammonium chlorate	$NH_4\ ClO_3$
Metal (or metal-acting).......*ites*	Sodium chlorite	$Na\ ClO_2$
	Ammonium chlorite	$NH_4\ ClO_2$
Metal (or metal-acting) *hypo..ites*	Sodium hypochlorite	$Na\ ClO$
	Ammonium hypochlorite	$NH_4\ ClO$
Metal (or metal-acting) *per...ates*	Potassium permanganate	$K\ MnO_4$

Representative salts. There are a great many more salts than acids and bases inclusively. Immense quantities of various salts occur in that vast conglomerate mixture which comprises the crust of the earth. And salts are of untold importance industrially and physiologically. For the present, however, only a few representative salts are listed below which are of interest for one reason or another:

Name of salt	*Formula*	*Common name, with suggestions as to use and occurrence*
Sodium chloride....	$NaCl$...........	The major and desired component of table salt.
Calcium chloride ...	$CaCl_2$	Also in table salt as an impurity.
Mercurous chloride..	$HgCl$...........	Calomel — a cathartic.
Mercuric chloride...	$HgCl_2$..........	Bichloride of mercury / Corrosive sublimate } a disinfectant.
Ethyl chloride......	C_2H_5Cl.........	An anesthetic.
Sodium bromide ...	$NaBr$	Used as sedatives — separately or mixed, as in "triple bromide."
Potassium bromide .	KBr	
Ammonium bromide	NH_4Br	
Sodium carbonate...	Na_2CO_3.........	Washing soda.
Sodium bicarbonate	$NaHCO_3$........	Baking soda.
Calcium carbonate..	$CaCO_3$..........	In limestone, in marble, and in chalk cliffs.
Ferrous carbonate...	$FeCO_3$..........	In Blaud's pills, a hematinic.
Silver nitrate.......	$AgNO_3$	Lunar caustic.
Sodium nitrite......	$NaNO_2$.........	Used to decrease blood pressure.
Calcium phosphate..	$Ca_3(PO_4)_2$.......	The major salt component of bones and teeth.
Calcium sulfate.....	$CaSO_4$..........	One of the salts causing "hard water."
Magnesium sulfate..	$MgSO_4$..........	Epsom salt.
Sodium stearate.....	$NaC_{17}H_{35}CO_2$....	Component of soap.
Zinc stearate.......	$Zn(C_{17}H_{35}CO_2)_2$..	A dusting powder.
Glyceryl stearate....	$C_3H_5(C_{17}H_{35}CO_2)_3$	Stearin — a fat.

This is just a preliminary study of bases, acids, and salts. More, much more, will be said concerning these important compounds as time goes on.

Questions

1. What radical is common to all acids? What is the name and composition (in general) of the associated radical? Illustrate by reference to a list of at least ten acids.

2. What radical is common to all bases? What is the composition of the associated radical? Illustrate by reference to a list of at least ten bases.

3. How does an alcohol differ in composition from an inorganic base? Illustrate by reference to specific examples.

4. What radicals contribute to salts? Illustrate by reference to at least ten salts not mentioned in this chapter.

5. Why is red litmus called a base indicator and blue litmus an acid indicator? Are these infallible tests for the presence of acids or bases? Why?

6. How do the acids included within each of the following groups differ from one another in composition?

   a. Hydrosulfuric acid, sulfuric acid, and sulfurous acid.

   b. Hydrochloric acid, hypochlorous acid, chloric acid, and perchloric acid.

   c. Nitric acid and nitrous acid.

CHAPTER XII

Valence

Let us now continue with the study of measurements from a chemical angle, this time: *factually*, the combining capacities of atomic weights of elements and of radical weights as they are combined within molecular weights of compounds; *theoretically*, the combining capacities of atoms and atom groups as they are combined within molecules of compounds.

Combining capacities of atomic weights of elements. ***They are fixed values.*** The fact has been stressed several times that the composition of the molecular weight of a compound, as represented in its formula, is always the same; and this is consistent with the Law of Definite Weight Proportions. The reason for this is that atomic weights of elements have definite combining capacities in respect to each other; and these combining capacities must meet an exact balance between the elements concerned in assembling the compound.

For some elements combining capacities of their atomic weights are fixed values, regardless of the elements with which they enter into combination, and regardless of combining conditions. For other elements, combining capacities of their atomic weights vary, depending in part upon the specific elements with which they are combined and in part upon other conditions, but they are always constant for the same elements under the same combining conditions. For example:

The *atomic weight* of hydrogen (1.008) has a *fixed combining capacity* and chemists have adopted the practice of using this as the measuring basis for capacities of the atomic weights of other elements. One shorthand method for representing this condition makes use of the symbol for the atomic weight with a dot, or dash, or some other device for indicating the *extent* of the combining capacity.	*Represented thus* H' meaning that the atomic weight of hydrogen has a combining capacity of *one*.

The atomic weight of sodium (22.997) and The atomic weight of potassium (39.096)	always have the same constant combining capacity, which is *equal* to that of hydrogen.	Na' K'

The atomic weight of oxygen (16)	always has the same combining capacity which is *twice* that of the atomic weight of hydrogen.	O''

	With hydrogen or metal elements as partner elements within compounds, it always has *twice* the combining capacity of the atomic weight of hydrogen;	S''
But the atomic weight of sulfur (32.06) has a variable combining capacity.	when it has oxygen as a partner element, sometimes it has *four* and	S''''
	sometimes *six* times the combining capacity of the atomic weight of hydrogen.	S''''''

Valence as to atomic weights and importance. The label that has been given to this combining capacity of elements is *valence.* Therefore, from now on, when so inclined, instead of saying "combining capacity of the atomic weight of the element," we shall just say "valence of the element."

Since it is the valence of elements that is the fundamentally important factor that determines the quantitative make-up of compounds, it follows that, given a knowledge of valences as to atomic weights of various elements, one should be in a position to reason one's way to the composition of molecular weights of many compounds. Here are examples, with reasonings:

		Represented thus
Hydrogen has a valence of. . 1 Oxygen has a valence of. . . . 2	therefore, the molecular weight of water must contain 2 atomic weights of hydrogen to 1 atomic weight of oxygen.	$H_2'O''$
Sulfur in sulfur dioxide has a valence of. . . . . 4 Oxygen has a valence of. . . . 2	therefore, the molecular weight of sulfur dioxide must contain 1 atomic weight of sulfur to 2 atomic weights of oxygen.	$S''''O_2''$
Sulfur in sulfur trioxide has a valence of. . . . . 6 Oxygen has a valence of. . . . 2	therefore, the molecular weight of sulfur trioxide must contain 1 atomic weight of sulfur to 3 atomic weights of oxygen.	$S''''''O_3''$

There will be more practice with this functioning of valence presently.

Valence as to radicals composed of two or more elements. Thus far valence has been discussed only in respect to atomic weights of elements, but it applies also to the combining capacities of radical weights that are composed of two or more elements, such as the nitrate and sulfate radicals. Radicals of this order always have fixed, never variable, valences in reference to this adopted measuring standard: namely, the combining capacity, or valence, of the atomic weight (1.008) of hydrogen. Thus:

	Represented thus
Nitrate radical weight has a valence of 1.	NO_3'
Sulfate radical weight has a valence of 2.	SO_4''
Phosphate radical weight has a valence of 3.	PO_4'''

Importance. Obviously, with a knowledge of valences of such radicals one is in a position to anticipate the composition of molecular weights of compounds that contain them. For example:

As to the composition of hydrogen sulfate:

Since hydrogen has a valence of 1 and sulfate a valence of 2	the molecular weight of hydrogen sulfate must be composed of 2 atomic weights of hydrogen to 1 sulfate radical weight.	*Represented thus* $H_2{}'SO_4{}''$

As to the composition of calcium phosphate:

Since calcium has a valence of 2 and phosphate a valence of 3	the molecular weight of calcium phosphate must be composed of 3 atomic weights of calcium to 2 phosphate radical weights.	*Represented thus* $Ca_3{}''(PO_4)_2{}'''$

Valence of some such radicals accounted for. The inclusive valence of such a radical is really a measure of the valence that is not satisfied between the elements within the same. With some radicals this valence is easily accounted for, not so with others. Thus:

1. The inclusive valence of the nitrate radical is 1.............. $(NO_3)'$
But within this radical the valence of each oxygen is 2, and that of nitrogen is 5 .... $(N'''''O_3{}'')'$
Evidently, then, the total valence carried by the oxygen within the radical is *six*, against that carried by the nitrogen which is only *five*. Therefore, there is a left-over valence of *one* between the oxygen and nitrogen and it is this which constitutes the unsatisfied valence of the nitrate radical as a whole and which must be satisfied by some other element.

2. Again, the valence of the sulfate radical is 2................ $(SO_4)''$
But within this radical the valence of each oxygen is 2 and of sulfur is 6 .... $(S''''''O_4{}'')''$
Accordingly, the total valence carried by the oxygen inclusively is *eight*, against the valence of *six* carried by the sulfur. Hence, the left-over valence of *two* is the valence of the sulfate radical, to be satisfied by combination with some other element.

But the valence of some radicals is not thus easily accounted for. Among these are acid radicals of organic acids such as acetate and tartrate (p. 142); and the student is advised just to accept the valences of these radicals as they stand without, at present, attempting to account for them.

Definition of valence from a factual view point. *Valence is the combining capacity of the atomic weight of an element, or of the radical weight of two or more combined elements, measured in reference to the combining capacity of the atomic weight of hydrogen (1.008) with an accepted valence of one.*

Positive and negative valence. Elements and radicals within compounds either actually carry or have an inclination toward carrying either positive or negative charges of electricity. Moreover, the two elements or radicals that contribute to any given compound carry opposite and equal charges, with the result that

the compound itself is neutral. Within hydrogen chloride, for example, hydrogen has a tendency toward carrying a positive charge of electricity, the chloride has a tendency toward carrying an equal quantity of negative electricity. Again, in sodium sulfate, the sodium is positively charged while the sulfate is negatively charged — both with equal quantities of electricity, although of opposite varieties.

Extent of charges. The extent of positive or negative charges of electricity that atomic weights of elements and radical weights either actually carry or have a tendency to carry have been experimentally determined and it has been found that they are commensurate with their respective valences. Accordingly:

When within compounds,[1] atomic weights of hydrogen, calcium, and aluminium carry, respectively, one unit, two units, and three units of positive electricity; or, as the chemist frequently says, hydrogen has a valence of *one-positive*, calcium a valence of *two-positive*, and aluminium a valence of *three-positive*.	*Represented thus* H^+ Ca^{++} Al^{+++}
Within acids and salts in which they comprise the entire acid radical, atomic weights of chlorine, bromine, and iodine carry one unit each of negative electricity, while that of sulfur carries two units of negative electricity. Or, as the chemist puts it, chlorine, bromine, and iodine have a valence of *one-negative*, while sulfur has a valence of *two-negative*.	*Represented thus* Cl^- Br^- I^- S^{--}
The ammonium radical weight carries one unit of positive electricity; the nitrate, sulfate, and phosphate radical weights carry, respectively, one unit, two units, and three units of negative electricity. In other words, ammonium has a valence of *one-positive*, nitrate a valence of *one-negative*, sulfate a valence of *two-negative*, and phosphate a valence of *three-negative*.	*Represented thus* NH_4^+ NO_3^- SO_4^{--} PO_4^{---}

Importance of positive and negative valences. It is, of course, this tendency of elements and radicals toward acquiring positive or negative charges when within compounds that determines what elements and radicals will and will not combine with each other, since only elements and radicals with inclination toward carrying opposite charges have a mutual combining interest. Again, it is the extent of the positive and negative charge carrying capacity, or valence, that determines the number of atomic weights of elements and of radical weights that will enter into said combinations to make compounds.

Valences listed and put to work. In the table on page 142 there is a listing of some of the elements and radicals, their valences and

[1] For the present, for the sake of simplifying matters, we shall regard all elements and radicals as actually carrying these charges of electricity when combined within compounds.

shorthand devices for same, that will appear more or less frequently in compounds with which we shall be dealing as we proceed with the further study of chemistry throughout this text. A more extensive list is given on the back cover of the text.

The functioning of these valences, by way of making it possible to reason one's way to the composition of compounds, is no different from reasonings presented previously (p. 140), save that this time the positive and negative tendencies of elements and radicals are taken into consideration. For example:

As to the composition of potassium carbonate. Since the atomic weight of potassium carries one unit of positive electricity, or has a valence of *one-positive,* and carbonate radical weight carries two units of negative electricity, or has a valence of *two-negative,* the molecular weight of potassium carbonate is composed of 2 atomic weights of potassium and 1 carbonate radical weight.	*Represented thus* $K_2^+CO_3^{--}$
More briefly — as to composition of aluminium sulfate. Since aluminium has a positive valence of three and sulfate has a negative valence of two, the molecular weight of aluminium sulfate is composed of 2 atomic weights of aluminium and 3 sulfate radical weights.	*Represented thus* $Al_2^{+++}(SO_4)_3^{--}$

Valences of Elements and Radicals

Hydrogen	H^+	Oxygen	O^{--}		
		Hydroxyl	OH^-		
Metal elements		***Acid radicals***			
Potassium	K^+				
Sodium	Na^+	Chloride	Cl^-		
Silver	Ag^+	Bromide	Br^-		
Cupric	Cu^{++}	Sulfide	S^{--}		
Calcium	Ca^{++}			Chlorite	ClO_2^-
Magnesium	Mg^{++}	Chlorate	ClO_3^-	Hypochlorite	ClO^-
Zinc	Zn^{++}			Perchlorate	ClO_4^-
Ferrous	Fe^{++}	Nitrate	NO_3^-	Nitrite	NO_2^-
Ferric	Fe^{+++}	Sulfate	SO_4^{--}	Sulfite	SO_3^{--}
Chromium	Cr^{+++}	Carbonate	CO_3^{--}		
Aluminium	Al^{+++}	Phosphate	PO_4^{---}	Phosphite	PO_3^{---}
Metal acting radicals		***Organic acid radicals***			
Ammonium	NH_4^+	Acetate	$C_2H_3O_2^-$		
Methyl	CH_3^+	Tartrate	$C_4H_4O_6^{--}$		
Ethyl	$C_2H_5^+$	Stearate	$C_{17}H_{35}O_2^{--}$		

Valence as to atoms and atom groups. Valences of atomic weights of elements and radical weights are *factual findings;* they have been discovered as the result of a great deal of careful and painstaking experimental investigations. But the inquiring

mind wants a *why* for this phenomenon of valence. However, as on a number of previous occasions when seeking "whys" for factual findings, it must be admitted that the scientist does not really know the answer. Consequently once again, one must turn to believed-in atoms of elements in believed-in molecules of compounds to satisfy this natural and estimable curiosity.

And the reasoning, in general, is that the character of charge, positive or negative, and the extent of the measurable valences that are *known* to be carried by atomic weights of elements and by radical weights within molecular weights of compounds are presumably determined by the character of the charge and the number of ultimate and not-possible-to-measure valence charges that, *in theory*, are believed to be carried by atoms of elements within molecules of said compounds. For example:

	Representation	
Within molecular weights of compounds, and in terms of *large valence units* of positive and negative electricity *carried by atomic weights and radical weights:*	*Valences of atomic weights and radical weights*	
Valence of atomic weight		
of hydrogen (1.008) is 1 positive (large unit),	H^+	
of calcium (40.08) is 2 positive,	Ca^{++}	
of chlorine (35.457) is 1 negative,	Cl^-	
of oxygen (16) is 2 negative.	O^{--}	
Valence of radical weight		
of nitrate (62.008) is 1 negative (large unit),	NO_3^-	
of sulfate (98.06) is 2 negative.	SO_4^{--}	
Because		
Within molecules of compounds, and in terms of *ultimate valence units* of positive and negative electricity *carried by atoms* and *atom groups:*		*Valences of atoms and atom groups*
Valence of each atom		
of hydrogen is 1 positive (ultimate unit),		H^+
of calcium is 2 positive,		Ca^{++}
of chlorine is 1 negative,		Cl^-
of oxygen is 2 negative.		O^{--}
Valence of each atom group		
of nitrate is 1 negative (ultimate unit)		NO_3^-
of sulfate is 2 negative.		SO_4^{--}

Thus it is that the valences as listed on p. 142 apply not only to *known* valences for atomic weights of elements and for radical weights but also to *believed-in* valences for atoms and atom groups. Therefore, with such a valence table at hand — or much better with this information memorized *correctly* — one is in a position not only to reason one's way to the actual composition of molecular

weights of many compounds but also to anticipate the supposed composition of molecules of said compounds. For example — and stressing only extent of valence, not kind of charge:

In regard to water:

It is *known* that in reference to atomic weights, the valence of the atomic weight of hydrogen is 1; the valence of the atomic weight of oxygen is 2; therefore, the *molecular weight* of water must contain *2 atomic weights* of hydrogen to *1 atomic weight* of oxygen; represented thus, H_2O.	It is *believed* that in reference to atoms, the valence of the atom of hydrogen is 1; the valence of the atom of oxygen is 2; therefore, the *molecule* of water must contain *2 atoms* of hydrogen to *1 atom* of oxygen; represented thus, H_2O.

Valence defined theoretically. From a *factual* angle valence has already been defined (p. 140), but not from the theoretical angle. Therefore, *theoretically,* valence is the combining capacity of the atom of an element or of an atom group inclusively measured in reference to the combining capacity of the atom of hydrogen with an ultimate valence of one.

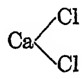
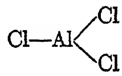
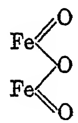
PLACEMENT OF ATOMS WITHIN MOLECULES

As has been said previously most scientists believe thoroughly in the existence of molecules and of atoms within them. Of course, molecules and atoms may in very truth exist in nature, but, if so, they have not revealed themselves to man with unquestionable certainty and until that time comes molecules must still remain firmly believed-in, not known-to-be, ultimate particles of substances; while atoms must remain firmly believed-in, not known-to-be, ultimate particles of elements within said molecules.

Some items of belief have already been considered, among them relative weights of molecules, relative weights of atoms, and relative valences of atoms as a factor in determining the composition of the molecule.

Another line of interest and speculation has to do with the *placement of atoms within molecules.*

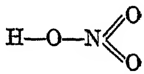
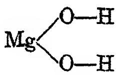
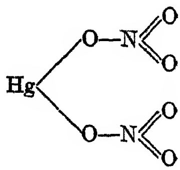
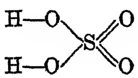
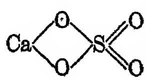
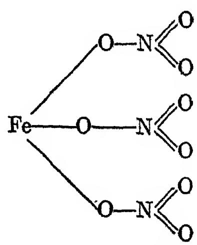
Guesses directed by facts. To begin with it should be said that the chemist does not picture the placement of atoms within the molecule in just any pattern of his fancy, but rather looks to that which is *known* concerning the way elements build themselves into the molecular weight of the compound concerned to help point the way as to how things may *perhaps* be mapped out on the part of the atoms within the molecule. Here are some examples of such reasonings:

Valences of atomic weights of elements in respect to each other	*Valences of atoms of elements in respect to each other*	*Placement of atoms in the molecule which will meet these relative valences on the part of the atoms concerned*
It is *known* that the *molecular weight* of calcium chloride contains 1 atomic weight of calcium, valence 2, and 2 atomic weights of chlorine, valence 1. $Ca''Cl_2'$	Therefore, it is *believed* that the *molecule* of calcium chloride contains 1 atom of calcium, valence 2, and 2 atoms of chlorine, valence 1. $Ca''Cl_2'$	
It is *known* that the *molecular weight* of aluminium chloride contains 1 atomic weight of aluminium, valence 3, and 3 atomic weights of chlorine, valence 1. $Al'''Cl_3'$	Therefore, it is *believed* that the *molecule* of aluminium chloride contains 1 atom of aluminium, valence 3, and 3 atoms of chlorine, valence 1. $Al'''Cl_3'$	
It is *known* that the *molecular weight* of ferric oxide contains 2 atomic weights of iron, valence 3, and 3 atomic weights of oxygen, valence 2. $Fe_2'''O_3''$	Therefore, it is *believed* that the *molecule* of ferric oxide contains 2 atoms of iron, valence 3, and 3 atoms of oxygen, valence 2. $Fe_2'''O_3''$	

The structural formula. Such pictured placements as are given above are called *structural formulas* and they *represent proposed placement of atoms in relation to each other within molecules of the compounds concerned, also the relative valences of the atoms therein.* It will be noted that in these, as in all structural formulas, valence, or valence bonds as they are frequently called, are represented by lines, the character of charges — positive or negative — not being indicated.

For molecules containing three elements. The three structural formulas presented above are for molecules which contain only *two* varieties of atoms in correspondence with compounds which are composed of only two elements. Now for structural formulas for molecules of bases and of such acids and salts as are believed to contain three varieties of atoms. These, of course, must be in respect to the compounds concerned which are known to be composed of three elements.

It is *known* that within bases the hydrogen and oxygen are in close combination with each other and can easily be taken intact from one base to become part of another base. Likewise it is *known* that the nonmetal and oxygen which comprise an acid radical, such as in the nitrate and sulfate radicals, are in similar close combination and can be taken intact from one acid or salt to become part of another acid or salt. Hence it is *believed* that molecules of all bases must contain one or more identical hydroxide atom groups in which the oxygen and hydrogen atoms are in close combination; that molecules of all sulfates must contain one or more identical sulfate atom groups in which the sulfur and oxygen atoms are in close combination; and that molecules of all nitrates must contain one or more identical nitrate atom groups in which the nitrogen and oxygen atoms are in close combination. Structural formulas for some of these compounds are as follows:

The compound with empirical formula	*Structural formula*	*The compound with empirical formula*	*Structural formula*
Sodium hydroxide $Na'(OH)'$	Na—O—H	Nitric acid $H'(NO_3)'$	
Magnesium hydroxide $Mg''(OH)_2'$		Mercuric nitrate $Hg''(NO_3)_2'$	
Sulfuric acid $H_2'(SO_4)''$			
Calcium sulfate $Ca''(SO_4)''$		Ferric nitrate $Fe'''(NO_3)_3'$	

But why, says the student, do so much guessing about the inside of molecules which may not even exist; why not just take compounds as they are and let the make-believe alone? The intelligent, inquiring mind, however, does not work that way, even in respect to the most ordinary happenings of everyday life. Such a mind is continually seeking reasons as to why things are as they are, and until the real reasons are discovered, imaginary reasons, if good ones, are quite satisfying.

So to the chemist, it is most satisfying when excellent guesses are possible as to the way atoms build themselves into molecules. And certain it is that a good comprehension on the part of the student of the significance of these guesses, which fit in so admirably with the facts concerning compounds, is accompanied automatically by a better acquaintance with said compounds, the way they really are and the way they behave.

Questions

1. a. Why, factually, is the valence of potassium 1? Of magnesium 2? Of aluminium 3? Of carbon 4?
   b. How, theoretically, are these valences accounted for?

2. Why, factually, are the valences of the sulfide radical, the hydroxide radical, the carbonate radical, and the phosphate radical 2, 1, 2, and 3 respectively?

3. Making use of your knowledge of valences of the elements concerned assemble formulas for at least ten oxides.

4. Assemble formulas for at least ten bases, ten acids, and twenty-five salts, indicating the valences of the radicals, both as to kind and extent. Name the compounds thus represented.

5. What does a structural formula represent? Assemble first the empirical formula, then the structural formula, for the molecule of each of the following compounds: carbon dioxide, zinc oxide, phosphorus pentoxide, calcium hydroxide, ferric hydroxide, potassium hydroxide, hydrogen sulfide, hydrochloric acid, carbonic acid, barium nitrate, ferric sulfate, and sodium carbonate.

CHAPTER XIII

Within the Atoms of the Various Elements

Facts yet to be explained. Thus far we have been saying that elements behave thus and so as they enter into combination with each other to make compounds, presumably because their atoms behave thus and so as they enter into combination to make molecules. It has been said, for example: that (*fact*) some elements are disintegrating, not so other elements, because (*theory*) the atoms of some elements are disintegrating, but not atoms of other elements; that (*fact*) some elements, such as helium, have no tendency to enter into combination either with other elements or with themselves, because (*theory*) the atoms of such elements have no tendency to enter into combination with other atoms. And it has been said that (*fact*) elements are selective in their combining preferences — some elements having a tendency toward becoming positively charged, other elements negatively charged — because (*theory*) their atoms within molecules are so inclined; that (*fact*) atomic weights of elements exhibit definite measurable valences when combined within compounds, because (*theory*) their atoms exhibit definite valences as to each other when combined within molecules of said compounds.

But scientists have not been content to stop here. They say in effect: "So far, so good, but *why do atoms behave thus and so?*" For the answer it has become necessary to enter into the atoms themselves and consider the way things are supposed to be therein.

Of course, no theorizing is satisfying to the scientist unless it has its roots in factual findings. So it is that reasoned imaginings as to inner-atom conditions have actually grown out of discoveries from researches that have been among the most brilliant of all time. These researches include investigations in respect to radioactive elements that were being carried on in the 1890's by a French scientist, Henri Becquerel, and by Marie and Pierre Curie, and that have been continued down to the present time in experimental investigations by various other great scientists.

This study, however, will not attempt to enter into complexities of these researches nor will it consider by any means all of the

details of the inner-atom theory; it will only attempt to present such concepts of the theory as will provide partial answers, at least, to a few questions concerning the aforementioned behavior of atoms, hence of elements.

Structural features within atoms. Up to about 1895 atoms of all elements were quite generally believed to be ultimate bits of matter, different in respect to each other for the various elements but always compact, hard, impenetrable, and indestructible. But all this is entirely changed, since it is believed now that within the atom of every element there is a nuclear mass which occupies an exceedingly tiny portion of the space occupied by the atom as a whole. Outside this nucleus, at relatively vast distances from it — that is, in terms of measurements on an atomic scale — there are planetary bodies, distributed in some orderly placement scheme in respect to the nucleus and to each other (Fig. 36).

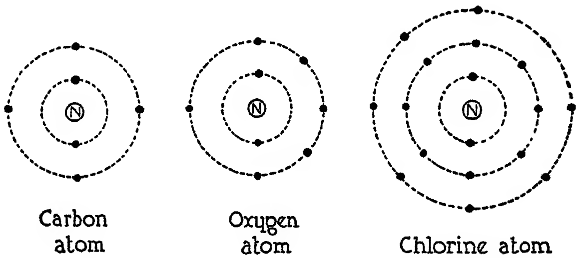


FIG. 36. An atom is composed of a nucleus surrounded by planetary bodies.

Thus it has come about that instead of being hard compact masses, it is now believed that atoms, within the confines of their boundaries, are really mostly space. It will be noted that these structural features as to atoms, on an exceedingly minute scale, are suggestive of the structural features of the solar system, on an exceedingly enormous scale, the sun as to the latter system being the nuclear mass with its revolving planets at vast distances from the same.

And atoms' planets are believed to be moving in orbits around their nuclei as are the solar planets around the sun, only much more rapidly, indeed with a speed of 150,000 miles per second, which approximates the speed with which light travels.

Varieties of particles. Although there are ninety-two different varieties of atoms, each of the ninety-two elements having an atom peculiar to it, nevertheless it is believed that nature uses but three kinds of particles for the making of all of these atoms.

One variety of particle is relatively heavy and carries an ultimate unit of positive electricity; it is called a *proton.* A second variety of particle is negligible in its weight as compared to the weight of a proton, and it carries an ultimate unit of negative electricity that is equal in value to the positive charge carried by a proton; the name given to this particle is *electron.* The third particle is neutral as to charge and is, therefore, called a *neutron;* it is believed by some to be composed of a proton and electron but embedded in each other; its weight is that of a proton.

The atom in its own right is neutral. Since there are ninety-two different atoms built of the same three varieties of particles, it becomes apparent that nature must use different numbers of protons, electrons, and neutrons for the building of these different atoms. But it is believed that in its own right, and aside from its neutrons, the *atom of each element has an equal number of protons and electrons.* For example:

Carbon Atom	*Oxygen Atom*	*Chlorine Atom*
6 protons	8 protons	17 protons
6 neutrons	8 neutrons	18 neutrons
6 electrons	8 electrons	17 electrons

This would mean that, when in possession of only its own family of electrons and protons, the atom as a whole is neutral.

THE NUCLEI OF THE VARIOUS ATOMS

Contributing particles. The nucleus of the atom of every element contains all of the atom's protons and neutrons but no electrons, save such as are embedded within neutrons. It follows, then, that

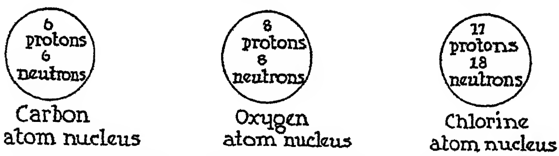


Fig. 37. Atom nuclei contain protons and neutrons.

since the weight of the electron is negligible the weight of the atom as a whole is that of its nucleus. It also follows that the nucleus of the atom carries a positive charge the extent of which is determined by the number of protons therein present. Thus, the nucleus of the carbon atom has the inclusive weight of its six protons and six neutrons, while its charge is the positive charge of its six protons; the weight of the nucleus of the chlorine atom

is that of its seventeen protons and eighteen neutrons, while its charge is that of its seventeen protons (Fig. 37).

Atomic number. Another very important item of belief is that *the number of free protons is the same for all nuclei of atoms of the same element and is peculiar to said atoms.* Thus it is that the number of free protons in the nuclei of the ninety-two different atoms is believed to vary from one proton in the nuclei of all hydrogen atoms to ninety-two protons in the nuclei of all uranium atoms.

Moreover, the number of protons which is peculiar to the nuclei of all atoms of the same element, called the *atomic number of the element*, is of exceeding importance because it is believed to determine the chemical nature of the atom, hence of the element concerned. Thus, the chemical nature of hydrogen is presumed to be due to the one nuclear proton in each of its atoms, or to its atomic number of one; the chemical nature of oxygen is presumed to be due to the eight nuclear protons in each of its atoms, or to its atomic number of eight. (See back cover of text for atomic numbers of elements.) Just how the atomic number of an element, or the number of free protons in its nucleus, determines the chemical behavior of atoms will be considered later.

Atoms of the same element can have different numbers of neutrons. Whereas the number of free protons within the nuclei of all atoms of the same element must be a constant, the same is believed not to be true of neutrons which can vary, at least for atoms of most elements.

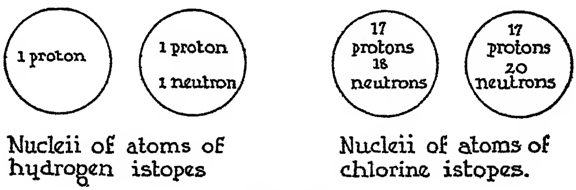


FIG. 38

For example, the nucleus of every "light hydrogen" atom contains only one proton, while the nucleus of every atom of "heavy hydrogen," called deuterium, contains one proton and one neutron (Fig. 38); but it should be observed that the atomic number of both of these hydrogen atoms is one (one proton); hence, although they do weigh differently, they behave alike in chemical ways.

Likewise, the nucleus of every "light chlorine" atom contains seventeen protons and eighteen neutrons, whereas the nucleus of every "heavy chlorine" atom contains seventeen protons and twenty neutrons; thus, again, while these atoms do weigh differently, they are identical atoms from a chemical angle since their atomic number (17 protons) is the same.

Atoms such as the two hydrogen atoms and the two chlorine atoms are called isotopes in respect to each other. Or, in general, from a theoretical angle, *isotopes* are atoms that have different numbers of neutrons in their nuclei, hence weigh differently, but have the same number of free protons; hence the same atomic number, as the result of which they behave alike chemically.

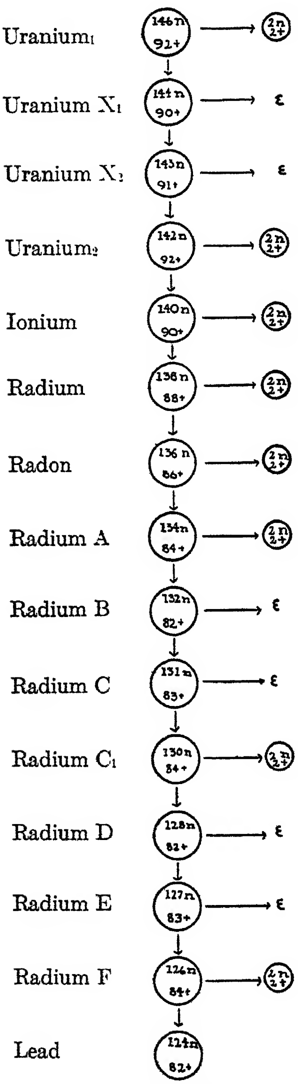


FIG. 39. Disintegration of Nuclei of Atoms beginning with that of Uranium

Nuclei of radioactive elements. ***A crowded condition.*** Since neutrons are neutral as to charge they do not mind being packed close to each other. But with protons this situation is different since they carry like charges and are, therefore, interested in getting far enough away from each other so that their mutual repulsion is not felt.

Now it will be recalled that nuclei of the various atoms occupy exceedingly minute portions of the atoms' respective volumes (p. 149). But even so, within nuclei of the lighter weight atoms there seems to be plenty of "elbow room" for their protons, although the chance of the same comfortable condition becomes increasingly less likely on the part of atoms with increasing numbers of protons. And so it happens that when it comes to nuclei of the heaviest atoms, namely those of the radioactive elements, the large number of protons within such limited space, even though separated as far as is possible by neutrons, are packed in so closely to each other that conditions are unbearable.

Fragments are ejected. To relieve this condition, such a nucleus ejects with great force a succession of nuclear fragments. One variety of fragment is believed to be composed of two protons and two neutrons and is the nucleus of a helium atom (Fig. 39). But while the ejection of each such particle does get rid of protons and thereby brings about a degree

of relief within the nucleus, at the same time it upsets the neutrality of the atom as a whole, which is likewise disturbing. As a result, the atom follows the ejection of the above variety of particle with an ejection of electrons, which sometimes may be obtained by the "explosion" of a neutron within the nucleus and sometimes may be thrown from the atom's external field.

Of course with each particle ejected from the nucleus, a new nucleus, hence a new atom, is made. And this violent throwing-off of a succession of nuclei of helium atoms and of electrons is believed to continue until an atom nucleus is left in which the remaining protons are able to get far enough away from each other so that an approximate degree of comfort is established. With uranium atom nucleus as the beginning nucleus, the series of ejections and the successive atom nuclei made are as represented in Figure 39. It will be noted that the end nucleus obtained from this series of eruptions is that of the lead atom. Eventually each helium atom nucleus is believed to "pick up" two planetary electrons to make a complete helium atom (Fig. 40).

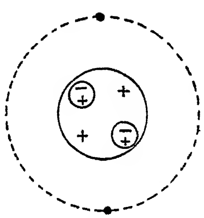


FIG. 40. A Complete Helium Atom

The fact of radioactivity explained. Thus is explained the radioactivity of certain elements, the cause of the same being, supposedly, the crowded condition as to protons within the nuclei of their atoms. Thus, too, are explained the alpha particles (positively charged) and the beta particles (negatively charged) that are known to be ejected from radioactive elements (p. 45), since it is believed that each alpha particle is the positively charged nucleus of a helium atom and each beta particle a negatively charged electron.

FIELD EXTERNAL TO THE ATOM'S NUCLEUS

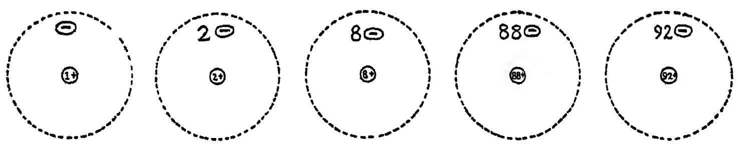
It will be recalled (p. 149) that within the fields external to the nuclei of the various atoms, the planetary bodies are relatively far apart; that they are in an orderly placement in respect to the nuclei, and are moving in definite orbits around the various nuclei with a speed that approximates that of light.

From now on, however, little, if anything, will be said further concerning the belief that these atomic "planets" do travel in orbits and with such tremendous speed. But, in passing, it is interesting to consider that, should this belief be true, an incon-

ceivable amount of kinetic energy must be bound up within the confines of the myriads of atoms within molecules of the thousands of substances possessed by earth.

But features to which more detailed attention will be given are the nature of planetary bodies, the number of "planets" common to all atoms of the same element, and their distribution. And finally, through the aid of this information, attempts will be made to find answers to the "whys" of certain chemical behaviors of atoms, hence of elements.

Planetary bodies, what are they and how many? Since all the atoms' protons and neutrons are within their nuclei, it follows that the atoms' planets must be electrons; and such is believed to be the case, each planet being a single electron. And inasmuch as atoms are neutral, when in possession of only their own electron families (p. 150), it is apparent that all atoms of the same element must have the same number of planetary electrons as there are free protons in their nuclei (Fig. 41).



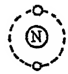
Hydrogen atom	Helium atom	Oxygen atom	Radium atom	Uranium atom
1 planetary electron	2 planetary electrons	8 planetary electrons	88 planetary electrons	92 planetary electrons
Atomic number 1	Atomic number 2	Atomic number 8	Atomic number 88	Atomic number 92

FIG. 41. The number of planetary electrons is the same as the number of free protons in the atom's nucleus.

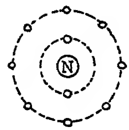
Thus, *atomic number* acquires another significance, since it can refer not only to the number of protons in the nuclei of all atoms of the same element, but also to the number of planetary electrons, the latter being really determined by the former.

Relative placement of planetary electrons. As for the relative placement of planetary electrons, as they move around the nuclei of atoms, it stands to reason that the greater the number of electrons the more complicated conditions must become. However, it is believed that nature follows the very orderly scheme of placing these electrons in from one to six successive "shells" in respect to the various nuclei, and that there are positions for only a definite number of electrons within each shell. The first four of these schemes are represented in Figure 42.

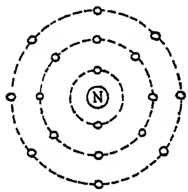
The first accepted placement scheme provides for 2 positions on opposite sides of the nucleus.



The second scheme provides for 10 positions distributed thus: 2 in the inner shell
8 in the second and outer shell.



The third scheme provides for 18 positions distributed thus: 2 in the inner shell
8 in the second shell
8 in the third or outer shell.



The fourth placement scheme provides for 36 positions: 2 in the inner shell
8 in the second shell
18 in the third shell
8 in the outer shell.

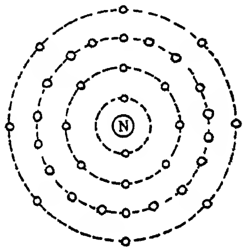
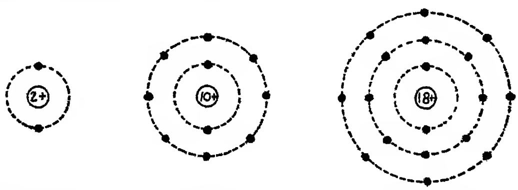


FIG. 42

The fifth and sixth placement schemes provide for 54 and 86 positions distributed in concentric shells as follows:

54 positions, distributed thus: 2, 8, 18, 18, 8.
86 positions, distributed thus: 2, 8, 18, 32, 18, 8.



Helium atom
Atomic number 2

Neon atom
Atomic number 10

Argon atom
Atomic number 18

FIG. 43. Three of the Six "Satisfied" Atoms

The six satisfied atoms. Now it is believed that all positions in these six placement schemes must be filled by planetary electrons if everything is to move along happily in the atoms' external fields; but it is obvious that only six varieties of atoms: namely, those with 2, 10, 18, 36, 54, and 86 planetary electrons, respectively, are able to meet this condition. And the atoms that are thus fortunate are those of helium, neon, argon, krypton, xenon, and radon (Fig. 43).

Chemical inertness of some elements explained. As a result, atoms of these six elements are completely self satisfied: they are neutral as to charge and they have one or another of the six just-right numbers of planetary electrons within their own families to fill all positions in the corresponding placements; therefore these atoms are not interested in the company of other atoms. And this fits in with the *factual* finding that the six elements — helium, neon, argon, krypton, xenon, and radon — are actually inert chemically, not being interested in entering into chemical combination either with themselves or with other elements.

Atoms of the other eighty-six elements. But what about the other eighty-six varieties of atoms, how do they distribute their not-just-right numbers of planetary electrons? And, as to this, they are believed to fill all positions possible with their own electron

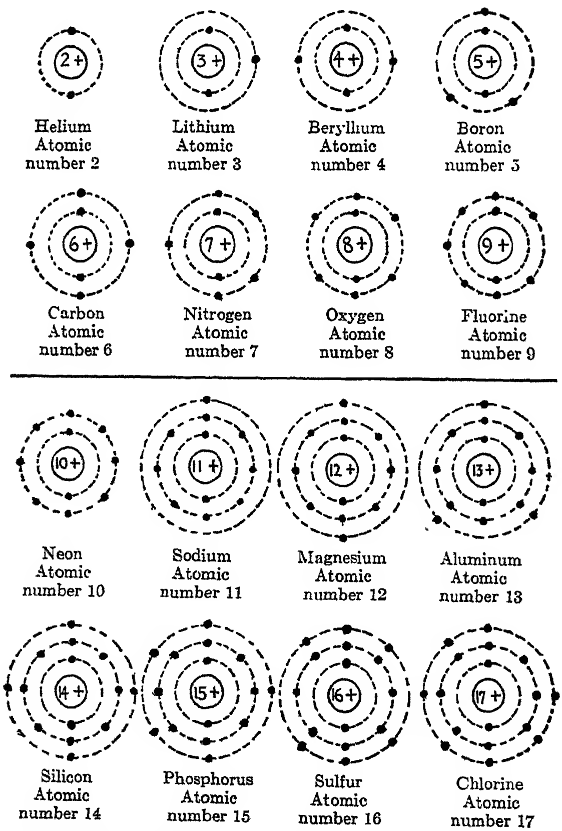


FIG. 44. Placements of Planetary Electrons in Two Series of Atoms

families, beginning with the two positions in the inner shell and proceeding successively to other shells, any electron-vacant positions being thereby obtained in the outer shell (or the two outer shells in the case of atoms with large numbers of planetary electrons). For example, the atoms with atomic numbers of from 2 to 9 and 10 to 17 inclusively distribute their planetary electrons as represented in Figure 44.

One variety of compensating adjustment. All of these atoms are content from the standpoint of their being neutral as to charge, and they are stable in respect to such shells as have all of their positions filled with electrons. But in the outer shell where there

The sodium atom prefers to lend the one electron in its outer shell; but the chlorine atom, with only one place to fill, prefers to borrow one electron. When such an arrangement has taken place, a sodium chloride molecule is made, the sodium atom having the positive charge of one extra proton and the chlorine atom a negative charge of one extra electron.

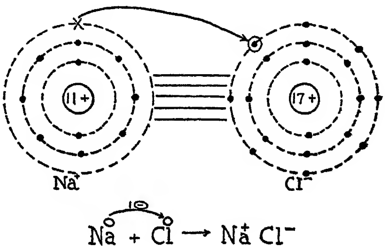
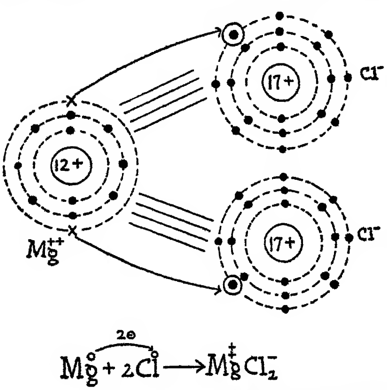


FIG. 45. The Making of a Molecule of Sodium Chloride

are vacant positions there is a condition of "strain." To relieve this "strain" two sorts of compensating adjustments are believed to be possible.

A mutual lending and borrowing of electrons. One of these adjustments involves either lending — to another atom or atoms — all electrons from the atom's outer shell or borrowing enough electrons to fill all vacant positions in said shell (Figs. 45 and 46).



When the atoms mutually concerned are magnesium and chlorine atoms, each magnesium atom upon ending the two electrons from its outer shell engages two chlorine atoms each of which claims one of these electrons to fit into one otherwise vacant position. A molecule of magnesium chloride becomes thereby established in which the one magnesium atom has a positive charge of two extra protons and each chlorine atom a charge of one extra electron.

FIG. 46. The Making of a Molecule of Magnesium Chloride

The atoms acquire a charge. Of course, upon lending one or more electrons the atom will be left with more protons back in its nucleus than planetary electrons, and will thereby acquire a positive charge the extent of which will depend upon the number of electrons loaned. And contrariwise, upon borrowing electrons the atom will at once have more electrons than protons and will acquire a negative charge commensurate with the number of electrons borrowed. But in either event this acquiring of a charge seems at times to be more satisfactory on the part of atoms thus affected than having a condition of strain due to electron-vacant positions in their outer shells.

In regard to the atom's choice, as to whether it will lend all electrons from its outer shell or borrow electrons to fill all vacant places, it seems to prefer to do that which will result in its acquiring the lower charge.

The molecule system established. When atoms of two or more elements have entered into such an electron lending and borrowing arrangement and have as a result acquired respectively positive and negative electric charges, they become at once mutually attracted and move up near each other to form a molecule group (Figs. 45 and 46).

Selectivity of elements and electrovalence explained. We are now in a position to answer questions as to why elements that do enter into combination are selective as to other elements with which they will combine; and why, when entering into said combinations they exhibit very definite valences as to kind and extent (pp. 140–142 and p. 157).

The first question finds an answer in the supposition that elements, such as sodium, magnesium, and aluminium, are not interested in combining with each other because their atoms all prefer to *lend* electrons from their outer shells, which means that upon doing so they all become positively charged, hence would repel rather than attract each other. On the other hand, certain other elements, such as oxygen, sulfur, and chlorine, are not interested in entering into combination with each other because their atoms all prefer to *borrow* electrons, which means that upon doing so they become negatively charged, hence likewise would repel each other. But such elements as sodium, magnesium, etc., do enter into combination with such elements as oxygen, chlorine, etc., because of the opposite preferences on the part of their atoms and the consequent opposite charges acquired by their atoms upon accomplishing their mutual lendings and borrowings.

As for the explanation of the extent of valence of the element, it is believed to be due to the number of electrons that the atom of the element lends or borrows. For example: atomic weights of elements sodium and magnesium have measurable valences of one positive and two positive, respectively, because the sodium atom (atomic number 11) and the magnesium atom (atomic number 12) are believed to prefer to lend their outer one and two electrons, and when this has taken place they are left respectively with one and two more protons than electrons.

Again, atomic weights of chlorine and oxygen have measurable valences of one negative and two negative because the atom of chlorine (atomic number 17) and the atom of oxygen (atomic number 8) prefer to borrow, respectively, one and two electrons into their outer shells, as the result of which the chlorine atom acquires one more electron and the oxygen two more electrons than they have protons.

The hydrogen atom. The atom of the element hydrogen must be considered by itself. The nucleus of this atom contains but

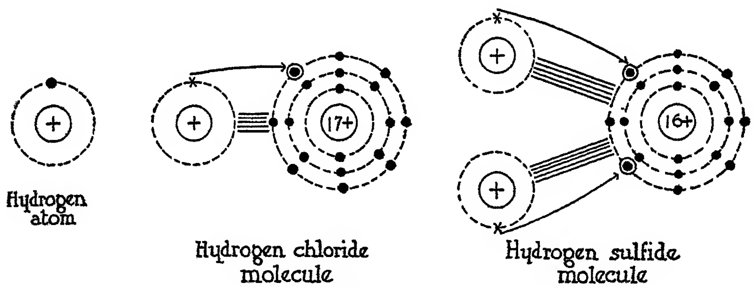


FIG. 47

one proton, which means that the atom has an atomic number of one, and there is, therefore, but one electron in its planetary field (Fig. 47). But upon entering into combination with other atoms it is believed that, instead of borrowing one electron thereby obtaining the desirable configuration in its planetary field that is like that of the satisfied helium atom, the hydrogen atom in some instances prefers to lend this one and only electron. When this happens only the hydrogen atom nucleus is left with its positive charge of one proton. And this is consistent with the fact in respect to the atomic weight of hydrogen, which upon combination with some elements is known to acquire a valence of one large unit of positive electricity.

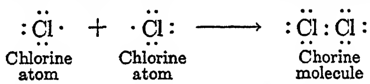
As should be expected, when a hydrogen atom or atoms have

loaned electrons they join the partner atoms in forming molecule groups (Fig. 47).[1]

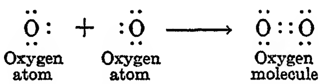
A second method of compensating adjustment. Another way that atoms have of compensating for electron-vacant positions in their outer shells is for two or more atoms to move up to each other in such a way that the complement of eight positions in the outer shell of each atom (a complement of two positions for each hydrogen atom) is satisfied by the plan of *sharing electrons.*

Molecules of simple substances and of many compounds are believed to become established from the atoms concerned by just such a sharing-of-electrons scheme. Here are examples (only electrons in the atoms' outer shells are represented):

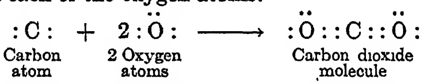
In making a molecule of chlorine the two chlorine atoms, each of which has 7 electrons in its outer shell, move up to each other in such a way that they *share one pair of electrons* between them. This gives each chlorine atom the desired 8 electrons in its outer shell. The dots are intended to represent only the number of electrons in the outer shell, not their distribution:



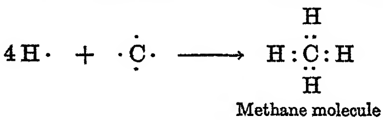
In making a molecule of oxygen, the two oxygen atoms, each of which has 6 electrons in its outer shell, move up to each other in such a way that they *share two pairs of electrons,* thereby giving each oxygen atom the desired 8 outer electrons. Again, dots represent electrons in the outer shell, not their distribution:

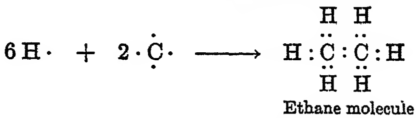


In making a molecule of carbon dioxide the carbon atom shares two pairs of electrons with each of the oxygen atoms:



This type of compensating adjustment is believed to take place in establishing molecules of many compounds that contain hydrogen atoms. Thus:





[1] Atoms of hydrogen and chlorine and of hydrogen and sulfur are believed to have engaged in this mutual lending and borrowing of electrons only when molecules of hydrogen chloride and hydrogen sulfide are in water solution. When within molecules of these substances in the gaseous state. these atoms engage in the second type of compensating adjustment (p. 160).

This arrangement gives each carbon atom the 8 electrons in its outer shell and each hydrogen atom 2 electrons. This is most satisfactory to the carbon atom, while for the hydrogen atom it produces the 2-electron condition comparable to that in the satisfied helium atom.

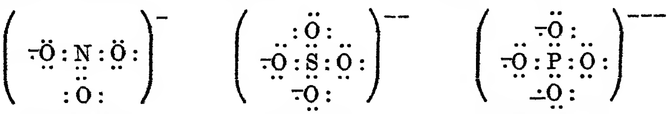
Covalence and the fact of neutrality of elements in some substances explained. This manner of compensation between atoms, discussed above, is after the plan of sharing electrons and is called *covalence.* Moreover, since the atoms mutually concerned have neither loaned nor borrowed electrons they maintain their neutral condition within the molecule group of atoms established.

Thus is explained another *fact:* namely, the fact that within simple substances and many compounds the contributing elements, while exhibiting their respective valences at to extent, actually are neutral as to charge. Accordingly:

Fact: chlorine element within chlorine simple substance is neutral; *theory:* because chlorine atoms within the chlorine molecule are neutral, and they are neutral because they fill vacant places in their outer shells by sharing electrons instead of lending and borrowing electrons.

Again, *fact:* within carbon dioxide the elements carbon and oxygen are neutral; *theory:* because carbon and oxygen atoms within carbon dioxide molecule are neutral, and they are neutral because they have completed their outer shells of 8 electrons by a mutual sharing of electrons — not by lending and borrowing electrons.

Covalence and radicals. While radical atom groups as a whole, such as the nitrate, sulfate, and phosphate, do exhibit electronegative valences, having borrowed electrons from atoms outside their own atom groups, it is believed that, other than through said borrowing, valence compensations between themselves within the atom groups are of the electron-sharing variety. This is represented in the following as to nitrate, sulfate, and phosphate atom groups. Shared electrons are represented, as usual, by dots, while borrowed electrons are represented by the negative sign:



Nitrate atom group — Sulfate atom group — Phosphate atom group

Of course, the borrowed electron or electrons constitute the valence of the atom group as a whole. Thus, the nitrate atom group has a negative valence of the one borrowed electron, the sulfate group a negative valence of two borrowed electrons; and this is in accordance with previous valence findings (p. 142).

Questions

1. Describe, in general, the conditions as they are believed to exist within (a) the nucleus of an atom; (b) the external field of an atom.
2. What, factually, is a radioactive element? Name three such. How, theoretically, is the radioactivity of these elements explained?
3. Hydrogen (light hydrogen) and deuterium (heavy hydrogen) are isotopic elements. What does this mean? In what respects are atoms of these elements believed to be alike and in what respects different from each other?
4. What is the atomic number of an element? On the basis of their respective atomic numbers account for the negative valence of two of sulfur, and for the positive valence of one of potassium.
5. Why, theoretically, are there no helium compounds?
6. When hydrogen reacts with chlorine to make hydrogen chloride, what changes do the participating atoms undergo?
7. What, in general, determines the electrovalence of the atom of an element as to kind and to extent?
8. Represent, diagrammatically, the mutual lending and borrowing of electrons between the atoms concerned that is required to establish a molecule of calcium chloride. A molecule of hydrogen sulfide.
9. In certain compounds the elements are not charged. Why, theoretically, are such compounds possible?
10. Illustrate, diagrammatically, the combination of electrovalence and covalence among the atoms concerned within the molecule of magnesium sulfate. Within the molecule of ammonium hydroxide.

CHAPTER XIV

A Study of Water

Water is a substance which nature provides so generously that the great majority of people just take it for granted and use it automatically without ever knowing how little they are really acquainted with it. It is proposed to give considerable attention to this indispensable substance, stressing some of its physical features of significance and some of the chemical reactions of importance in which it participates.

PHYSICAL PROPERTIES AND APPLICATIONS

Color, odor, and taste. With some of the physical properties of water everyone is acquainted. Everyone knows that it is colorless, odorless, and tasteless. These properties may have no great significance in human affairs but, since water is so prevalent and so continuously essential, perhaps it is just as well that it is thus inconspicuous in these respects.

As a solvent. Water is the best of all liquid solvents, meaning that more substances are able to dissolve in water to an appreciable extent than in any other liquid. It acts as a solvent in varying degrees; some substances it dissolves well, others not so well, and this is all to the good. Certainly it is a wise provision that *water is a good solvent for sugars,* since sugars can thereby be carried through cell membranes and distributed from here to there within plants. On the other hand it is also a wise provision that *water dissolves oxygen only slightly,* since most of earth's oxygen supply is thereby kept in the air for the use of land animals (p. 71).

Because of this solvent property, naturally occurring water is never pure. As it courses through the soil it dissolves various substances with which it comes into contact and carries them along in solution. To this is due varying tastes (palatable and otherwise) of water solutions in different localities. Certain salts, chiefly calcium and magnesium salts, collected in solution in this manner are responsible for so-called "hardness" of water (p. 204). When it is necessary to have water which is relatively free from dissolved salts and other substances it is customary to separate the water from said substances by the process of distillation.

The student should be able to cite other definite instances of importance in the concerns of earth and of man which are due to the fact that water dissolves this substance well, that substance not so well, and still other substances not even appreciably.

Temperature of maximum density. Once water has reached a temperature of 4° C. it behaves in a manner peculiar to itself in regard to the effect that further decrease in its temperature has on its volume change, hence on its density.

Most substances contract continuously as their temperatures go down farther and farther, hence they meet with continuously increasing densities as they get colder and colder. If, therefore, the substance is liquid and mobile, and if it is not at the same temperature throughout, an attempt at stratification will set in, with the lowest-temperature-portion of the liquid dropping down to the bottom, and the highest rising to the top (Fig. 48 A). *Such liquids* meet with their freezing temperatures at the bottom of their mass and *freeze from the bottom up.*

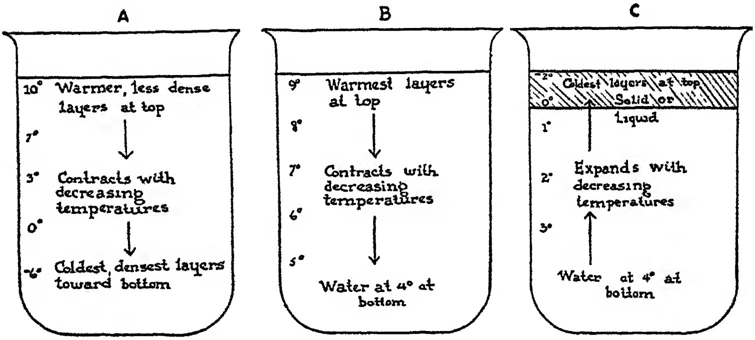


FIG. 48. Most liquid substances contract continuously, hence become increasingly more dense as their temperatures decrease. Water attains its maximum density at 4° C.

As for water, it behaves as do other liquids down to 4° C. in that as its temperature from any level above 4° is lowered it contracts continuously and becomes continuously denser *until it attains this temperature* (Fig. 48 B). But from 4° C. on down it behaves in a peculiar manner: instead of contracting as it gets colder and colder, it expands (Fig. 48 C). Therefore, *whether the temperature of water goes either up or down from this 4° level, it becomes lighter or less dense at both the higher and lower temperatures.* Important phenomena result from this peculiar property of water.

Interesting and important consequences. (1) *In summer*, as should normally be expected, the warmest layers of water in the pond or lake are at the top with colder and colder layers toward the bottom. This is a familiar fact to anyone who has dived into deep water in this season of the year.

(2) But, quite peculiarly to water, *in winter* the coldest water, or water at 0° C. or below, is at the top of the pond with warmer layers underneath and any water at 4° C. at the bottom (Fig. 48 C). Thus it is that *water freezes first at the top, then from there on down.* As a result, the floating layer of ice acts as an insulating cover above the warmer, liquid water underneath in which fish can live during the winter season. Only very shallow bodies of water ever freeze solid throughout.

(3) Finally, and most importantly, this maximum density of water at 4° C. which places colder, 0° C. water at the top is a *climate control factor*. If the reverse were true all water at 0° C. or below would be at the bottom of ponds and lakes where it would freeze. Under such conditions, during long cold winters, ponds and lakes might fill solid with ice from bottom to top and the heat of long, hot summers might not be able to melt it back to liquid water. Under these circumstances, eventually there might not be a temperate zone of successive summer and winter seasons but only winter throughout the year.

Freezing and boiling temperatures.[1] Water freezes at 0° C. or somewhat below this temperature. Water boils at 100° C. or somewhat above or below this temperature, depending upon the pressure upon its surface. Both of these temperatures are easy of attainment, and advantage is taken of this fact in practical ways. Thus, ice can be obtained easily for cooling purposes. If water is boiling one can depend upon its being in the vicinity of 100° C. should one desire such temperature for cooking or sterilizing. Steam can easily be obtained and, if in a closed container, raised to still higher temperatues for cooking more speedily and for the greater penetration desired for effective sterilization.

High specific heat of water. Less than two hundred years ago it was discovered by a Scotch chemist by the name of Joseph Black that different materials have different heat capacities, meaning that the same weights of different materials collect different quantities of heat in effecting the same temperature change. These heat capacities of materials are called their specific heats.

[1] See pages 3 and 4 for comparison with the other meanings for freezing and boiling points that make them exact, unvariable values.

Defined from a quantitative angle, with one gram of material and 1° C. temperature increase as the common measuring standards and the heat measured in calories (small): *specific heat or heat capacity of a material is the number of calories of heat which one gram of the material must collect to raise its temperature through 1° C.* The following are some representative specific heats which have been determined as the result of much careful experimentation:

Specific heat		*Meaning that, for raising its temperature through 1° C.*
Water	1.0	1 gram of water must collect 1 calorie of heat.
Alcohol	.5	1 gram of alcohol must collect ½ calorie of heat.
Air	.2	1 gram of air must collect ⅕ calorie of heat.
Aluminium	.2	1 gram of aluminium must collect ⅕ calorie of heat.
Iron	.1	1 gram of iron must collect 1/10 calorie of heat.

A more extensive table would only serve to impress still further that which is shown above: namely, that water must collect more heat for bringing about the same temperature change than do equal weights of other materials.

Or to get a different angle on this phenomenon, these findings make it possible to figure the *differing temperature increases that will be effected through collecting the same quantity of heat* on the part of these materials. Thus:

1 gram of water.....	on collecting 1 calorie of heat undergoes	1° C. temperature increase.
1 gram of grain alcohol	on collecting 1 calorie of heat undergoes	2° C. temperature increase.
1 gram of air........	on collecting 1 calorie of heat undergoes	5° C. temperature increase.
1 gram of aluminium	on collecting 1 calorie of heat undergoes	5° C. temperature increase.
1 gram of iron.......	on collecting 1 calorie of heat undergoes	10° C. temperature increase.

Some consequences. *Physiologically* this high heat capacity of water is of *vital* significance. Because of this property the water of the lymph and blood is able to collect, at the cells, the considerable quantity of heat made and carry it to the body surface, with less of a rise in temperature than would be the case if any other liquid than water had been provided by nature as the heat transportation medium. Suppose, by way of example, that alcohol (sp. ht. .5) were the transporting liquid medium, then for the same quantity of heat collected at the cells, either the temperature of this medium would be increased about twice as many degrees as

it is with water, or else the alcohol would be obliged to rush the collected heat to the surface of the body twice as fast, thereby giving the heart twice as much pumping to do.

A second climate control factor. Perhaps the chief reason why it is cooler near bodies of water than a few miles inland, during the summer, is because the heat capacity of water (sp. ht. 1) is so much greater than that of air and land (sp. ht. about .2). For example: of the portion of the day's heat which goes to a lake region, the water claims most of it for a *slight rise in temperature;* the rest is collected by the surrounding air and land for attaining approximately the same temperature increase. Farther inland, for an equal portion of the day's heat, with air and land as the chief collecting materials, their *temperature must rise higher* since their heat collecting capacities are so much less than that of the water of the lake. Herein lies one reason for the later spring around lakes and at the seashore than farther inland.

Man's uses of the high specific heat of water. Obviously the heat that is collected by water, or any other material, as its temperature rises, must be given up to the surroundings as its temperature goes down. Accordingly, it is the high specific heat of water that makes it so efficient for *heating buildings.* Down in the furnace the circulating water picks up an enormous quantity of heat—more than would any other liquid for the same temperature increase. Then later this water gives up this heat quantity for warming rooms to which it is conveyed.

And again, through the medium of the hot water bottle or hot flat iron, this rule of nature is taken advantage of *for securing comfort* in cold beds in the home and in therapeutic practice for patients. And the difference in the efficiency of these two devices lies in the differing specific heats of water and iron. The hot water or hot flat iron, put into the bed, must throw off as much heat in lowering its temperature from, let us say, 50° C. (122° F.) to 22° C. (72° F.) as it collected in increasing its temperature to this extent. Therefore, given the same weight of water and of iron, and the same temperature decrease, the water, since it had previously collected more heat than the iron, must have more to surrender. For example:

Specific heat of water is 1, therefore 1 gram of water loses 1 calorie of heat in lowering 1° C., 1000 grams of water in lowering 28° C. loses 28,000 calories of heat.

Specific heat of iron is .1, therefore 1 gram of iron loses .1 calorie of heat in lowering 1° C., 1000 grams of iron in lowering 28° C. loses 2800 calories of heat.

High latent heat of fusion of water. Another important discovery has revealed that as a substance changes from solid to liquid it must collect heat, but that the heat thus essential to melting disappears as heat since *it does not produce any temperature increase* as to the substance, the beginning solid and the resulting liquid being at the same temperature, if only just enough heat for the melting is provided. It is for this reason that this disappearing heat has come to be called *latent heat of melting or of fusion.* It has also been discovered that for its melting every substance — gram for gram or ounce for ounce — must absorb, or render latent, within the liquid its own definite heat quantity. Thus from a quantitative angle, with gram as the quantity of substance and calorie as the heat unit: *latent heat of fusion of a substance is the number of calories of heat which the substance must absorb in order to change 1 gram of said substance from the solid state to the liquid state without effecting any change in its temperature.*

The following are latent heats of fusion which have been experimentally obtained in respect to the substances specified:

Latent heat of fusion		*Meaning that:*
Water	79.71	79.71-calories of heat must be absorbed to change 1 gram of water solid at 0° C. to 1 gram of water liquid at 0° C.
Alcohol	24.9	24.9-calories of heat must be absorbed to change 1 gram of alcohol solid at − 114.4° C. to 1 gram of alcohol liquid at − 114.4° C.
Copper	42	42.0-calories of heat must be absorbed to change 1 gram of copper solid at 1083° C. to 1 gram of copper liquid at 1083° C.

And this short list serves to stress the facts concerned as well as would a longer list: namely, (1) each substance has its own latent heat of fusion; (2) *water has a relatively high latent heat of fusion.* And now what are some of the consequences which follow from the latter fact?

A third climate factor. In late winter or early spring, in regions around frozen-over lakes, once ice has collected enough heat provided by the sun during the lengthening days to raise its temperature up to 0° C., from then on, every gram of ice must collect 79.71 calories of heat just for its melting to liquid water still at 0° C. So at such times, much the greater portion of the day's heat in these regions is requisitioned by the great expanse of ice upon the lake just to accomplish its melting, leaving a smaller quantity of heat to be collected by the surrounding air and land for raising their temperature accordingly.

Farther inland, however, where there are but scattered and small quantities of ice, the major portion of the sun's heat during the day is collected by air and land whose temperatures, because of the low specific heats of these materials, rise considerably. Herein lies another reason (p. 167) why the advance of spring is slower around lakes than it is farther inland.

But as water freezes in the late fall, what must happen to the latent heat of fusion which it collected in the spring? And how does this affect the advance of fall around the lake in comparison with regions farther inland? Something for the student to think about!

Man devised uses. And man has learned how to put this high latent heat of melting of water to various uses, among them: *preservation of foods, making rooms more comfortable in summer*, and *therapeutic purposes*. Only in very small part is the *coldness* of ice responsible for the chilling of refrigerators and their contents and for the chilling of rooms, most of this cooling work being accomplished *during the melting* of the ice, as each gram of solid water takes the necessary 79.71 calories of heat from its environment and hides it away within itself as it becomes liquid water.

Again, the desired cooling from the application of the ice bag or ice pack — for easing headache, checking muscular contractions and infections, and for other therapeutic uses — is obtained only in very small part from the low temperature of the ice, but rather from the heat that is absorbed and lost temporarily as heat, as the ice at 0° C. changes to liquid water likewise at 0° C. And much of this heat for melting is taken from skin areas where the ice bag or ice pack is applied.

High latent heat of vaporization. Likewise when a substance changes from liquid to gaseous state it must absorb heat and, once again, this heat disappears as heat, the substance in the gaseous state being at exactly the same temperature as it was in the liquid state, that is, if only *just enough* heat is provided to bring about vaporization. The heat thus absorbed, and which remains hidden in the gaseous substance as long as said substance continues in this state, is called *latent heat of vaporization*, and it is definite in quantity for each substance at each temperature at which it vaporizes. Quantitatively defined, then: *latent heat of vaporization of a substance is the number of calories (small) of heat which 1 gram of the substance must absorb in order to change from liquid to gaseous state without undergoing any temperature change.* The heat of vaporization for some substances, including some values for water at

temperatures specified, are listed as follows and interpreted; and it should be noted that the latent heat of vaporization of water is very high:

Latent heat of vaporization	*Meaning that:*
Water at 0° C. 596 cal.	596 calories of heat must be absorbed to change 1 gram of water liquid at 0° C. to 1 gram of water gas at 0° C.
at 20° C. 584.9 cal.	584.9 calories of heat must be absorbed to change 1 gram of water liquid at 20° C. to 1 gram of water gas at 20° C.
at 40° C. 574.1 cal.	574.1 calories of heat must be absorbed to change 1 gram of water liquid at 40° C. to 1 gram of water gas at 40° C.
at 100° C. 539.5 cal.	539.5 calories of heat must be absorbed to change 1 gram of water liquid at 100° C. to 1 gram of water gas at 100° C.
Alcohol at 78° C. 204 cal.	204 calories of heat must be absorbed to change 1 gram of liquid alcohol at 78° C. to 1 gram of alcohol gas at 78° C.
Ether at 35.6° C. 83.9 cal.	83.9 calories of heat must be absorbed to change 1 gram of liquid ether at 35.6° C. to 1 gram of ether gas at 35.6° C.

Some consequences. *Physiologically* this high latent heat of vaporization of water is of vital significance in that it serves as one of the means whereby nature takes care of the considerable quantity of heat, from 2000 to 3500 Calories (large) per day, which is made in cells from kinetic or other energies previously required therein (p. 79). This heat is carried to the lung and skin areas, where nature disposes of it in two ways. (1) By far the larger portion is used for vaporizing the water which is excreted at these areas. In this manner approximately 574 calories of heat for vaporizing every single gram of this water at normal body temperature immediately becomes latent as heat, hence is responsible for no temperature increase whatsoever in these areas or the adjoining air. (2) A smaller portion of the heat, brought to body surfaces, is radiated as appreciable heat which, of course, keeps these areas warm and warms the surrounding air. Herein is provided the *major mechanism for body temperature control.*

Man devised uses. And just as man has learned to make latent heat of fusion of water work for him (p. 169) so, also, has he learned to put latent heat of vaporization to various good uses including its use for cooling purposes. Ever since prehistoric times natives of warm climates have known that water stored in a porous jar

and kept in a shady, breezy place becomes cooler. Why? A dampened sheet hung in a breezy, shady doorway cools the adjacent air. A cold water sponge cools the normal person, likewise the fever stricken patient. And again, why?

Finally. These are but some of the important functionings of these physical properties of water in the concerns of earth and man. There are other uses of these properties; and there are other physical properties which have received no mention. But even these limited considerations should serve to increase one's respect for water and its physical properties, for the ways in which nature has always used these properties, and the ways in which man has learned to use them.

CHEMICAL PROPERTIES AND APPLICATIONS

Composition. The formula for water makes it possible to figure readily the weight relationship that must always exist in respect to the hydrogen-oxygen composition of water. If the molecular weight quantity on any weighing basis whatsoever is the weight of water in question then the composition can be read directly thus:

18.016 *grams* of water are composed of
2.016 *grams* of hydrogen element and
16 *grams* of oxygen element.

18.016 *ounces* of water are composed of
2.016 *ounces* of hydrogen and
16 *ounces* of oxygen.

$$\underbrace{\underbrace{\overset{H_2}{2 \times 1.008}}_{2.016}\quad \overset{O}{16}}_{18.016}$$

But should the composition of other than molecular weight quantities of water be desired they can be figured from the weight relationship obtainable through said formula (p. 127).

Theoretically. Then there is that other functioning of the formula for water which has no practical value but is interesting from a theoretical angle: namely, the story it tells in respect to the supposed composition of the water molecule.

$$\underbrace{\overset{H_2}{\text{2 atoms}}\quad \overset{O}{\text{1 atom}}}_{\text{1 molecule}}$$

Molecular weight is a unit reacting weight. The molecular weight of water (18.016) is a *unit reacting weight* for this substance in that water participates in reactions in whole numbers times this weight, provided all associated substances, as well as water, are also measured in terms of their molecular weights. This fact is neatly represented in shorthand manner through equations for reactions in which molecular weights of water and other substances are represented by their formulas. Here are examples:

Water + Carbon dioxide ⟶ Carbonic acid
$H_2O + CO_2 \longrightarrow H_2CO_3$
1 × 18.016
1 molecular weight

Methane + Oxygen ⟶ Carbon dioxide + Water
$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$
2 × 18.016
2 molecular weights

Glucose + Oxygen ⟶ Carbon dioxide + Water
$C_6H_{12}O_6 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O$
6 × 18.016
6 molecular weights

Quantities of water in various reactions. The quantities of water and other participating substances that become mutually involved in any given reaction can, of course, be figured from the inherent reacting weight relationship obtainable through the agency of the formula equation for the reaction (p. 127).

Reactions involving water. The remainder of this study of water will treat of reactions that can be expected to set in upon the following contacts:

Water with metals
Water with metal oxides
Water with nonmetal oxides
Water in direct combination to make hydrates
Water in double decomposition or hydrolysis with salts

Metals in order of their chemical activities

Potassium
Sodium
Calcium
Magnesium
Aluminium
Zinc
Chromium
Iron
Nickel
Tin
Lead
(*Hydrogen*)
Copper
Mercury
Silver
Platinum
Gold

Water is a party to numerous reactions. Some of these reactions are a nuisance but, because of the unavoidably widespread occurrence of water, they take place whether one likes it or not. Hundreds of reactions with water as one of the substances concerned, however, are useful in one way or another: various cookery reactions include water as one party; all digestive reactions are between water and selected food compounds; many reactions that take place within the cells of plants and animals, and which are therefore of vital concern, involve water; and many reactions with water are of consequence in industrial processes.

Water with metals. In this connection we shall study first some reactions which *do* take place between *water and metals* and then sum up what to expect, in general, from such contacts. Here are some instances of actual happenings:

1. When a small piece of *potassium* is thrown on *water*, spread out for safety on a large plate, reaction sets in at once as the potassium, being lighter than water, darts here and there on the surface.

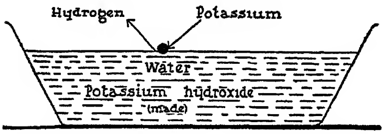


FIG. 49. Water in Reaction with Potassium

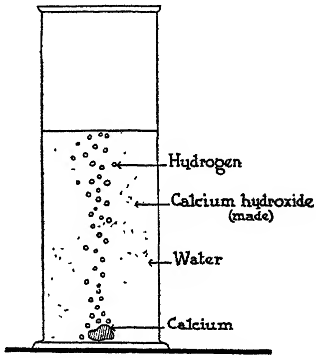


FIG. 50. Water in Reaction with Calcium

Hydrogen is made but begins to burn as soon as it gets into contact with oxygen of the air. *Potassium hydroxide*, a white soluble solid, is also made as is indicated when a strip of red litmus paper is dipped into the solution (Fig. 49):

$$\text{Water} + \text{Potassium} \longrightarrow \text{Hydrogen} + \text{Potassium hydroxide}$$
$$2\,HOH + 2\,K \longrightarrow H_2 + 2\,KOH$$

2. If exactly the same procedure is followed with a piece of *sodium* thrown on *water* on the plate, a similar reaction takes place with these differences (a) reaction is a little less speedy than with potassium, since sodium is less active than potassium (see accompanying list of metals); (b) frequently not enough heat is made to raise *hydrogen* to its kindling temperature; (c) *sodium hydroxide*, likewise a white, very soluble, solid substance, is the base made along with hydrogen:

$$\text{Water} + \text{Sodium} \longrightarrow \text{Hydrogen} + \text{Sodium hydroxide}$$

3. When *calcium* is the metal used and a small lump is dropped into *water*, calcium being denser than water drops to the bottom of the dish. But as soon as contact is made, a reaction similar to the two foregoing sets in, although it is slower because of the less activity of the calcium. *Hydrogen* is made, and a piece of red litmus dipped into the solution reveals the presence of a base, this time *calcium hydroxide* (Fig. 50):

$$\text{Water} + \text{Calcium} \longrightarrow \text{Hydrogen} + \text{Calcium hydroxide}$$

4. With *magnesium*, however, since this is a still less active metal than calcium, reaction with *water* is very slow at ordinary temperatures but proceeds appreciably, although still slowly, at temperatures around 60° C. and similar substances are made:

$$\text{Water} + \text{Magnesium} \longrightarrow \text{Hydrogen} + \text{Magnesium hydroxide}$$

But if magnesium and water are raised to still higher temperatures, then *magnesium oxide*, not magnesium hydroxide, is made:

$$\text{Water} + \text{Magnesium} \longrightarrow \text{Hydrogen} + \text{Magnesium oxide}$$

By this time one would be justified in beginning to wonder whether water in contact with *all* metals will result in similar reactions. This query will find an answer presently. Thus far only contacts such as are encountered in the laboratory have been dealt with. But what about such contacts as:

Water with aluminium,
Water with iron,
Water with nickel?

And the student on recalling everyday experiences may say: "I am on familiar ground now, and I am quite certain that no reaction occurs either between water and aluminium or between water and iron, because we have used aluminium and iron kettles for boiling water at home for years and they do not get any thinner!" But:

5. As to the *aluminium* dish and *water*, if the student thinks a bit further, the whitish layer which collects on the aluminium will be recalled. And the fact is that this is a layer of *aluminium oxide* which sticks so tightly to the remaining aluminium that the sharp edges of steel wool must be used to scrape it off. *Hydrogen* is also made, but so slowly that one is not ordinarily aware of

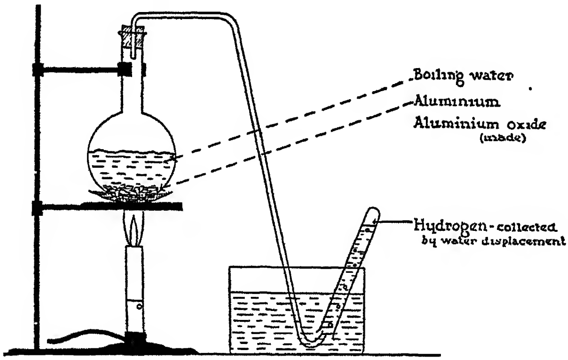


FIG. 51. Boiling Water in Reaction with Aluminium

it. However, if the aluminium is ground up to increase considerably the surface of contact with the water, and if the reaction is enclosed and the hydrogen collected, evidence can thereby be obtained that this gaseous substance actually is made (Fig. 51). It follows that aluminium kettles do get thinner as time goes on, although slowly:

$$\text{Water} + \text{Aluminium} \longrightarrow \text{Hydrogen} + \text{Aluminium oxide}$$

6. As for *iron* and *water*, iron being less active than aluminium (again, see list of metals, p. 172), reaction with boiling water, or at a temperature around 100° C., is inappreciable. Accordingly, the iron kettle handed down through generations of families does not seemingly get thinner. But if *steam* is obtained

and heated to 300° or 400° (superheated steam) and if the *iron* is ground to a powder, thereby increasing greatly the surface of contact between the steam and iron, reaction does take place appreciably, although slowly, and an appreciable quantity of *hydrogen* is made together with *magnetic iron oxide* (Fig. 52):

$$\text{Water} + \text{Iron} \longrightarrow \text{Hydrogen} + \text{Magnetic iron oxide}$$
$$4\,H_2O + 3\,Fe \longrightarrow 4\,H_2 + Fe_3O_4$$

Water in contact with iron at such temperatures is not commonly encountered, but whenever such contacts are obtained, as would be the case if iron pipes were used to convey superheated steam, slow reaction would most certainly set in.

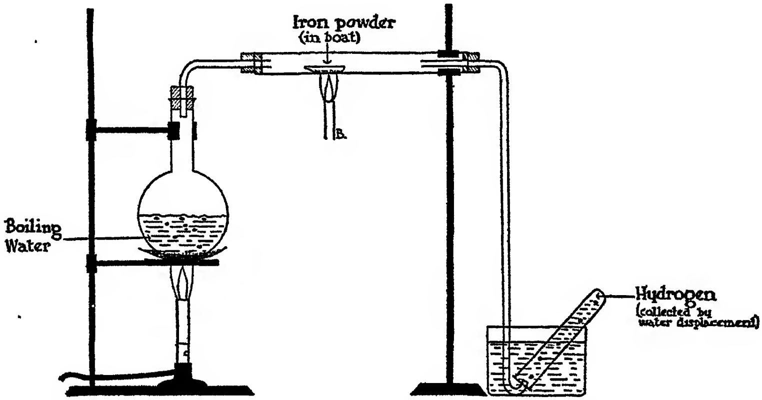


Fig. 52. Superheated Steam in Reaction with Iron. When the apparatus becomes filled with steam the second burner (B) is used to heat the iron powder and water in the combustion tube, thus bringing the iron in contact with superheated steam.

7. *Of practical concern.* Since higher and still higher temperatures are necessary for appreciable reactions between *water and nickel, water and tin,* and *water and lead* (why?), the advisability becomes apparent of selecting nickel or copper (see below) instead of aluminium or iron for making sterilizers; and lead, instead of iron, for making pipes intended to convey superheated steam in the industries.

But when we get down to copper we meet with a decided change in the story. For the fact is that *none of the metals "below hydrogen"* (p. 172) *gives any reaction whatsoever with water* no matter how high the temperature obtained. Thus:

Water (superheated steam) + Copper (of sterilizers) ⟶ *No* reaction
Water (boiling) + Silver (of spoons, etc.) ⟶ *No* reaction
Water (even at very high temperatures) + Platinum ⟶ *No* reaction
Water (even at the highest temperatures) + Gold ⟶ *No* reaction

Herein lies one reason why, when metals are listed in the order of their chemical activities, hydrogen is placed in the position

indicated, since the metals listed above this position, or as the chemist says, "metals above hydrogen," behave differently from "metals below hydrogen."

And so it becomes possible now to draw conclusions in regard to what reactions one can and cannot expect to take place from water with metals, as follows, in brief general statements:

$$\underset{\text{(below hydrogen)}}{\text{Water} + \text{Metal}} \longrightarrow \text{Hydrogen} + \underset{\substack{\text{(if at}\\ \text{ordinary}\\ \text{temperatures)}}}{\text{Base}} \quad \text{or} \quad \underset{\substack{\text{(if at}\\ \text{elevated}\\ \text{temperatures)}}}{\text{Metal oxide}}$$

$$\underset{\text{(below hydrogen)}}{\text{Water} + \text{Metal}} \longrightarrow \text{No reaction}$$

With these simple general statements memorized and with such a list of metals as is given on page 172 at hand, one is in a position to judge, with a pretty good chance of being correct, as to: (1) whether water does or does not react with this or that metal substance; (2) whether ordinary or high temperatures are necessary for appreciable reactions when such are possible; and (3) what products to expect, if any.

Water with metal oxides. Next for a study of possible reaction happenings between water and metal oxides. One such contact has been encountered several times in previous chapters and the reaction concerned is represented in the following equation:

$$\begin{array}{ccccc} \text{Water} & + & \text{Calcium oxide} & \rightarrow & \text{Calcium hydroxide} \\ H_2O & + & CaO & \longrightarrow & Ca(OH)_2 \end{array}$$

This reaction is as it should be since, in general, one can expect water to react with any metal oxide to make the corresponding base, a fact which holds for a metal oxide of a metal below hydrogen as well as of a metal above hydrogen:

$$\text{Water} + \text{Metal oxide} \rightarrow \text{Base}$$

Some such reactions are represented in the following word equations:

$$\text{Water} + \underset{\text{(very soluble)}}{\text{Sodium oxide}} \xrightarrow{\text{extensive reaction}} \text{Sodium hydroxide}$$

$$\text{Water} + \underset{\text{(slightly soluble)}}{\text{Magnesium oxide}} \xrightarrow[\text{reaction}]{\text{slight but appreciable}} \text{Magnesium hydroxide}$$

$$\text{Water} + \underset{\text{(negligibly soluble)}}{\text{Copper oxide}} \longrightarrow \text{Copper hydroxide (in negligible quantity)}$$

In medicinal practice a mixture of magnesium oxide and water is used to make the base magnesium hydroxide in the treatment of gastric hyperacidity (p. 192). Contacts of this variety which are

most commonly encountered *in everyday concerns* are: water with iron rust (ferric oxide) of rusty iron utensils or implements, and water with aluminium rust (aluminium oxide) of dulled aluminium ware. But due to the insolubility, meaning negligible solubility, of these metal oxides, reactions from these contacts are very slight:

Water + Ferric oxide → Ferric hydroxide
(negligibly soluble) (in negligible quantity)
Water + Aluminium oxide → Aluminium hydroxide
(negligibly soluble) (in negligible quantity)

Water with some nonmetal oxides. Water reacts with some, but not all, nonmetal oxides to make acids:

Water + (some) Nonmetal oxides → Acids

Perhaps *the most important of such reactions* is that between water and carbon dioxide to make carbonic acid.

Water + Carbon dioxide → Carbonic acid

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

Since carbon dioxide is always present in the atmosphere, such portions as get into solution react with some of the water after the foregoing manner. Thus it is that streams, rivers, ponds, and lakes are very dilute solutions of carbonic acid. *Physiologically* this reaction is of *vital* importance; it takes place continuously wherever carbon dioxide (p. 80) is made in the body cells. Consequently, this making of carbonic acid within the cells themselves or in the adjacent lymph or blood is a physiological factor to be reckoned with.

Other reactions of this variety are represented as follows:

Water + Sulfur dioxide → Sulfurous acid
Water + Sulfur trioxide → Sulfuric acid
Water + Phosphorus trioxide → Phosphorous acid
Water + Phosphorus pentoxide → Phosphoric acid

Some of these reactions are of industrial importance. The reaction between water and sulfur trioxide is of considerable importance because it is necessary to the making of sulfuric acid after the most used method (p. 61). That between sulfur dioxide and water is of importance because the resulting sulfurous acid is used for bleaching and as a preservative (p. 275).

Water in direct combination to make hydrates. ***What are hydrates?*** Hydrates are complex compounds, which is one way of saying that the chemist finds them difficult to explain. Seemingly within a hydrate the given compound and water are in

"loose" combination and ready to break away from each other with slight encouragement. This "loose" combination is commonly represented after the manner indicated in the following formula in respect to copper sulfate hydrate:

Formula for copper sulfate hydrate or blue vitriol — $CuSO_4 \cdot 5\,H_2O$. This translated means *factually*, that one molecular weight of copper sulfate hydrate is composed of one molecular weight of copper sulfate in combination with five molecular weights of water. *Theoretically*, this formula means that one molecule of copper sulfate hydrate is believed to be composed of one molecule of copper sulfate in combination with five molecules of water.

Salt hydrates. Salt hydrates are made more or less readily by direct combination between water and the salts concerned:

$$\text{Water} + \text{(many) Salts} \rightarrow \text{Hydrates (of given salts)}$$

Here are some examples:

1. When *copper sulfate* is dissolved in *water* such a reaction sets in within the solution, and if the excess water is evaporated carefully crystals of blue copper sulfate hydrate, commonly called blue vitriol, appear. The equation for the reaction is as follows:

$$\begin{array}{lclcl} \text{Water} & + & \text{Copper sulfate} & \longrightarrow & \text{Copper sulfate hydrate} \\ 5\,H_2O & + & CuSO_4 & \longrightarrow & CuSO_4 \cdot 5\,H_2O \end{array}$$

2. The making of plaster of Paris casts involves just such a reaction. When plaster of Paris, which is already partially hydrated *calcium sulfate* $[(CaSO_4)_2 \cdot H_2O]$, is mixed with *water* further reaction with water takes place and the completely hydrated salt or gypsum is made:

$$\begin{array}{lclcl} \text{Water} & + & \text{Plaster of Paris} & \longrightarrow & \text{Calcium sulfate hydrate or Gypsum} \\ 3\,H_2O & + & (CaSO_4)_2 \cdot H_2O & \longrightarrow & 2\,CaSO_4 \cdot 2\,H_2O \end{array}$$

Some incidental items of importance. *An energy product.* From such reactions an energy product in the form of *heat* is made along with the hydrate. This is due to the fact that the hydrate possesses less chemical energy than do the anhydrous salt and water inclusively. And anyone who has made a plaster of Paris cast has been aware of this heat product:

$$\begin{array}{ccccccc} \text{Water} & + & \text{Plaster of Paris} & \longrightarrow & \text{Gypsum} & & \\ \downarrow & & \downarrow & & \downarrow & & \\ \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & \longrightarrow & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \text{Heat} \end{array}$$

A reversible reaction. These reactions are reversible since hydrates decompose to make water and anhydrous salts. For appreciable decomposition of some hydrates a fairly high temperature is necessary. Thus, when copper sulfate hydrate is heated it decomposes:

$$\text{Copper sulfate hydrate} \longrightarrow \text{Water} + \text{Copper sulfate}$$

If a plaster of Paris cast is "baked" in the oven the gypsum decomposes, first to make plaster of Paris and, eventually, the completely dehydrated calcium sulfate:

$$\text{Gypsum} \longrightarrow \text{Water} + \text{Calcium sulfate}$$

Efflorescent hydrates. Certain hydrates decompose readily even at ordinary temperatures. Such hydrates are called "efflorescent." For example: sodium sulfate hydrate is highly efflorescent, that is, it decomposes readily at ordinary temperatures, leaving the anhydrous sodium sulfate. For this reason it is difficult to keep this hydrate for any length of time save in sealed containers.

Washing soda hydrate or sodium carbonate hydrate and borax hydrate or sodium borate hydrate are somewhat efflorescent, hence portions of these crystalline hydrates after standing around for a month or so in open containers will have decomposed, leaving behind the anhydrous powdery washing soda and borax.

Hydrates of substances other than salts. Salts are not the only substances which react with water to make hydrates. An outstanding example is the marked tendency of sulfuric acid to react in this manner. It is for this reason that concentrated sulfuric acid is used as a drying agent (p. 270) for products of reactions that are laden with undesired moisture, since the concentrated hydrogen sulfate combines with this water, thus removing it most effectively:

Hydrogen sulfate + Water ⟶ Hydrogen sulfate hydrate
(Sulfuric acid)

$$H_2SO_4 + 2\,H_2O \longrightarrow H_2SO_4 \cdot 2\,H_2O$$

Caution. In this instance a *large quantity of heat product is made* along with the hydrate. This constitutes a hazard in the laboratory where water solutions of sulfuric acid are frequently made from the concentrated acid. Consequently, when making such solutions, the experienced laboratory worker has learned to habitually *pour the denser concentrated acid very slowly into the less dense water* so that automatically a greater distribution of acid and water is obtained and the heat product thereby distributed.

Hydrates of common occurrence	*Common names*	*Formula for molecular weight and molecule*
Calcium chloride hydrate ...		$CaCl_2 \cdot 6\,H_2O$
Calcium sulfate hydrate.....	Plaster of Paris	$(CaSO_4)_2 \cdot H_2O$
Calcium sulfate hydrate.....	Gypsum	$CaSO_4 \cdot 2\,H_2O$
Copper sulfate hydrate......	Blue vitriol or Blue stone	$CuSO_4 \cdot 5\,H_2O$
Ferrous sulfate hydrate.....	Copperas	$FeSO_4 \cdot 7\,H_2O$
Sodium borate hydrate.....	Borax (hydrate)	$Na_2B_4O_7 \cdot 10\,H_2O$
Sodium carbonate hydrate...	Washing soda (hydrate)	$Na_2CO_3 \cdot 10\,H_2O$
Sodium sulfate hydrate.....	Glauber's salt	$Na_2SO_4 \cdot 10\,H_2O$
Magnesium sulfate hydrate..	Epsom salt (hydrate)	$MgSO_4 \cdot 7\,H_2O$
Potassium aluminium sulfate hydrate..................	Alum	$KAl(SO_4)_2 \cdot 12\,H_2O$
Hydrogen sulfate hydrate...		$H_2SO_4 \cdot 2\,H_2O$

WATER IN HYDROLYSIS REACTIONS

What is hydrolysis? Since our next studies have to do with the specific variety of reaction called *hydrolysis*, it would be well to have a definition of this sort of reaction before proceeding further. *Hydrolysis*, then, *is a double decomposition reaction* (p. 17) *involving water as one of the reacting substances.* In such reactions water functions as hydrogen hydroxide, half of its hydrogen constituting a hydrogen radical, the rest of its hydrogen and all of its oxygen serving as an hydroxyl radical.

Water in hydrolysis with salts. When water and a salt engage in hydrolysis the hydrogen radical from water combines with the acid radical from the salt to make an *acid product;* at the same time the hydroxyl radical combines with the metal radical to make a *base product:*

$$\text{Water (as Hydrogen hydroxide)} + \text{Salt} \longrightarrow \text{Acid} + \text{Base}$$

However, with many salts, for reasons that we shall not enter into at this time, only a portion of each salt seemingly reacts thus with water. As a result, some salt always remains in solution

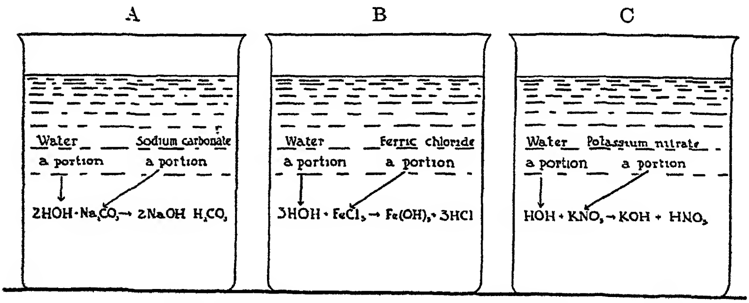


FIG. 53. Water in Hydrolysis with Salts

together with the base and acid made. Hydrolysis reactions with the salts sodium carbonate, ferric chloride, and potassium nitrate are represented in Figure 53.

A number of facts worthy of consideration follow from the foregoing findings as follows:

Four compounds are always present. The relative quantity of the salt which reacts with the water depends upon the particular salt. With some salts the reaction does not get very far, in which case there will be present within each solution a relatively high concentration of the remaining salt and a low concentration of the base and acid products. With some salts, the reaction is carried

almost to completion until very little of the initial salt remains, while concentrations of the base and acid products will be relatively high.

But in either event four substances are always present within the solution as follows:

the remaining *water*	considerable in quantity because of the great excess water used to obtain the solution;
the remaining *salt*	more or less in relative quantity, depending upon the particular salt;
the *base* product and the *acid* product	in relative quantities that depend upon the extent of the reaction.

For example: from reactions within solutions of the aforementioned salts (p. 180), these four compounds are as indicated in A, B, and C in Figure 54.

Within solutions in which salt hydrolyses are occurring, important consequences follow from the comparative character of the acid and base products, that is, whether the base is strong and the acid weak, or vice versa, or whether they are both strong.

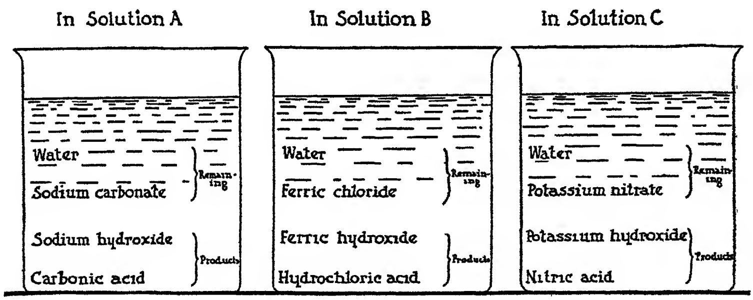


FIG. 54. In a water-salt solution four substances are always present.

If the base is strong (p. 238) ***and the acid is weak.*** Within such a solution, although the acid is indeed present, its effect is counteracted by the presence of the strong base. *The solution is, therefore, "basic in reaction,"* meaning that if tested with pink and blue litmus the presence of the base will be revealed but not that of the acid; and this base will react like a base regardless of the presence of the other three compounds. Such a condition is obtained in solution A (Fig. 54).

Note. — Because of the comparative character of these products, sodium carbonate and other salts responsible for similar results are sometimes incor-

rectly called bases. But these salts are by no means bases, although they do react with water to make *strong bases* and *weak acids*. The following is a list of some commonly used salts which react with water in hydrolysis to make such associated products:

Sodium carbonate	Salts that are "water softeners" (p. 205)	Potassium carbonate	
Sodium phosphate		Potassium phosphate	
Sodium borate		Potassium borate	
Sodium stearate	Salts of hard soap mixture	Potassium stearate	Salts of soft soap mixture
Sodium palmitate		Potassium palmitate	
Sodium oleate		Potassium oleate	
Sodium bicarbonate (baking soda)		Potassium bicarbonate	
Sodium acetate		Potassium tartrate	

Important consequences. (1) *Physiologically.* A salt that is always present in solution in the lymph and blood in considerable quantities is *sodium bicarbonate.* And one of the means whereby the reaction of these fluids is maintained a little on the basic side of neutral in the living animal is due to the hydrolysis reaction between water and this salt to make sodium hydroxide, a strong base, and carbonic acid, which is weak:

$$\text{Sodium bicarbonate} + \text{Water} \longrightarrow \text{Sodium hydroxide} + \text{Carbonic acid}$$
$$NaHCO_3 + HOH \longrightarrow NaOH + H_2CO_3$$

(2) *Therapeutically.* Sodium bicarbonate is frequently prescribed for correction of temporary hyperacidity of the stomach. It reacts with water in hydrolysis to make sodium hydroxide, as represented in the above equation, then this base reacts with some of the hydrochloric acid of the gastric juice to reduce the acidity of the gastric contents:

$$\text{Sodium hydroxide} + \text{Hydrochloric acid} \longrightarrow \text{Water} + \text{Sodium chloride}$$
$$NaOH + HCl \longrightarrow HOH + NaCl$$

(3) *In cleansings.* Sodium carbonate and sodium phosphate are put into hard water for the purpose of reacting with substances therein that render water thus hard and undesirable for cleansings. Toward this useful end these salts give excellent service. But when these "softening agents" are carelessly added in excess of quantities necessary to remove the offending hardness, *this excess* of either sodium carbonate or sodium phosphate reacts now with the water to make the strong base sodium hydroxide:

Softening agents		*Strong base*	*Weak acid*
Sodium carbonate + Water	$\longrightarrow$	Sodium hydroxide +	Carbonic acid
Sodium phosphate + Water	$\longrightarrow$	Sodium hydroxide +	Phosphoric acid

And although this base when made from salt hydrolysis is always in very dilute solution, it can be present in sufficient concentration

to produce an irritating effect on the skin, weaken fibers of silk and wool fabrics, and alter colors that are sensitive to such attacks.

Salts of soap mixtures also react with water to make strong bases and weak acids, but in these cases the sodium hydroxide or potassium hydroxide is made in such exceedingly low concentration that the skin, and silk and wool of fabrics are affected very little.

Soaps				*Strong bases*		*Weak acids*
Sodium stearate	+	Water	⟶	Sodium hydroxide	+	Stearic acid
Sodium palmitate	+	Water	⟶	Sodium hydroxide	+	Palmitic acid
Potassium oleate	+	Water	⟶	Potassium hydroxide	+	Oleic acid

If the acid is strong and the base weak. The hydrolysis of some salts results in each instance in the making of a strong acid and a weak base. Within such a solution, although the base is indeed present, it is the acid product this time which makes itself evident, and the *solution is said to be "acid in reaction,"* meaning that if tested with pink and blue litmus the presence of the acid is revealed but not that of the base.

Some salts which react thus with water together with the reactions concerned are as follows:

The salts				*Weak bases*		*Strong acids*
Silver nitrate	+	Water	⟶	Silver hydroxide	+	Nitric acid
Copper sulfate	+	Water	⟶	Copper hydroxide	+	Sulfuric acid
Ferric chloride	+	Water	⟶	Ferric hydroxide	+	Hydrochloric acid
Ammonium chloride	+	Water	⟶	Ammonium hydroxide	+	Hydrochloric acid

Salts of this character do not appear in the everyday concerns of most people but they must be reckoned with in the laboratory; because, certain it is that when put into solution water does react with such salts, with the result that the experimenter will be dealing, not only with the remaining salt, but also with the weak base and strong acid products likewise present.

If the base and acid are both strong. Finally there are some salts that react with water in hydrolysis to make strong bases and strong acids. Such salts are called neutral salts, since *solutions in which the hydrolyses take place are "neutral in reaction,"* meaning that, when tested with both acid and base indicators, such as red litmus and blue litmus, the presence of neither acid nor base is indicated.

Two salts of this variety and the hydrolysis reactions in which they participate are as follows:

The salts				*Strong base*		*Strong acid*
Sodium chloride	+	Water	⟶	Sodium hydroxide	+	Hydrochloric acid
Potassium chloride	+	Water	⟶	Potassium hydroxide	+	Hydrochloric acid

The first of these salts, sodium chloride, is, of course, the one used so prevalently in cookery; it is also the salt of highest concentration in the lymph and blood of animals. The second of these salts, potassium chloride, is present within the cells in higher concentration than is the sodium chloride. But, although water does react with them in hydrolysis to make the strong acids and strong bases specified, nonetheless the "reaction of the solution" in these locations is not affected thereby.

Water in hydrolysis with some food compounds. All digestive reactions involving carbohydrates, fats, and proteins are hydrolysis reactions, with water of necessity as one of the substances always participating. But, save for the little that will be said here concerning this process as to fats, these hydrolysis studies will be left until later (Chapter XXIX).

Water in hydrolysis with fats. Fats are salts, consequently their digestive reactions with water are after the manner of all salt hydrolyses.

Composition of fats and representative fats. Fats are *salts* which contain the glyceryl radical, which is common to all fats, and fatty acid radicals; the only variable on the part of different fats, therefore, is in respect to their fatty acid radicals. The following are three representative fats together with formulas for their molecular weights and molecules:

	Formula for molecular weight and for molecule
Glyceryl stearate	$C_3H_5(C_{17}H_{35}CO_2)_3$
Glyceryl palmitate	$C_3H_5(C_{15}H_{31}CO_2)_3$
Glyceryl oleate	$C_3H_5(C_{17}H_{33}CO_2)_3$

Fat hydrolysis. Since the metal-acting radical of all fats is the glyceryl radical, the base product made on their hydrolysis is always *glyceryl hydroxide;* the acid product varies with the specific fat, but it must always be a fatty acid.[2] Thus in brief summary statement:

A Fat + Water ⟶ Glyceryl hydroxide + A Fatty acid
or
Glyceryl alcohol
or
Glycerol
or
Glycerine

[2] Fatty acids are acids whose acid radicals contribute to fats.

When applied in respect to glyceryl stearate the reaction is as represented in the following equation:

$$\text{Glyceryl stearate} + \text{Water} \longrightarrow \text{Glyceryl hydroxide} + \text{Stearic acid}$$
$$C_3H_5(C_{17}H_{35}CO_2)_3 + 3\,HOH \longrightarrow C_3H_5(OH)_3 + 3\,HC_{17}H_{35}CO_2$$

Speed of fat hydrolysis. The speed of these reactions between water and fats is negligible at ordinary temperatures without catalytic aid, and they proceed very slowly even at very high temperatures without such aid. Outside the body, catalysts for speeding up these reactions are either dilute strong acids or dilute strong bases; inside the body, nature provides an excellent catalyst for such purpose in steapsin, a lipase which is made in the pancreas and sent on into the intestine, where it performs this mission.

More will be said as to fat hydrolysis when the hydrolysis of other food compounds is studied in later chapters.

Questions

1. What are some of the important uses of water as a solvent?

2. Compare the quantity of heat given off by 1 Kilogram of water in a hot water bottle at 44° C. (about 115° F.) with that of an "iron" of the same weight and temperature as each cools to 37° C. (98.6° F.). Which, therefore would be the greater source of heat?

3. How much heat must be "absorbed" from the body and the surrounding environment for melting 100 grams of ice within an ice cap? Once the ice begins to melt, what will be the temperature maintained within the ice cap as long as ice and water are in contact with each other? In what two ways then, does an ice cap function as a cooling agent? Which of them is the more effective?

4. How much heat must be "collected" from an ice box and contents during the melting of 10 Kilograms (about 22 pounds) of ice?

5. How much heat must disappear as latent heat of vaporization for the evaporation of one liter of water of perspiration?

6. Summarize in concise statements the chemical behavior of water in respect to each of the following: metals, metal oxides, nonmetal oxides, certain salts in direct combination, and salts in hydrolysis. Illustrate each reaction possibility through word and formula equations for typical contacts.

7. What is hydrolysis? Illustrate in reference to the hydrolysis of potassium phosphate and glyceryl oleate, a typical fat.

8. What determines whether the "reaction" of a salt solution will be "acid," "basic," or "neutral"? Illustrate by reference to solutions of potassium phosphate, ammonium chloride, and magnesium sulfate.

9. Why is it impossible to secure a high concentration of sodium hydroxide with a solution of sodium bicarbonate? What practical advantages are taken of this fact?

10. Why is copper a preferred metal for use in lining utensils subjected to superheated steam, as in autoclaves? From the standpoint of contact with water, which would be more durable for pressure cookers, aluminium or steel? Why?

11. What reaction is involved in the "setting" of a plaster of Paris cast? How do you account for the disappearance of water as the cast "sets"? Also account for the fact that there is seldom complaint of chilliness during the hardening process, as is frequently the case with moist applications.

12. If directions for preparing a solution call for a definite weight of a salt which you find occurs both as a powdery anhydrous salt and as a crystalline hydrate, will it make any difference in the concentration of the resulting solution as to which of these you select for use? Explain.

CHAPTER XV

Acids, Bases, Salts — Their Reactions and Applications

This chapter carries further a study which was begun in Chapter XI: namely, the study of the three important classes of compounds, *acids, bases, and salts.*

ACIDS WITH METALS AND METAL OXIDES

In review. The composition and naming of acids together with some representative acids, also the effect of acids with blue litmus, should be reviewed thoroughly at this time (pp. 133–135).

When metals are listed in the order of their comparative chemical activities (see accompanying list), and when hydrogen is included in the position indicated, those metals "above hydrogen," meaning metals which are more active than hydrogen, react with acids differently from those metals "below hydrogen." Therefore, this study will deal with reactions that can be *expected* to take place, first from contacts of acids with metals above hydrogen, then from contacts of acids with metals below hydrogen.

Potassium
Sodium
Calcium
Magnesium
Aluminium
Zinc
Chromium
Iron
Nickel
Tin
Lead
Hydrogen
Copper
Mercury
Silver
Platinum
Gold

Acids with metals above hydrogen. If a series of tubes containing zinc is set up and solutions of various acids added, as specified in Figure 55, it will be found that in every instance hydrogen element is displaced from the acid by zinc element with the result that gaseous hydrogen substance is made and the respective zinc salts. The hydrogen, being insoluble, bubbles out as rapidly as it is made; the salts, being more or less soluble and colorless, do not become evident unless one pours off the solution and evaporates the water. Word and formula equations for two of these reactions are as follows:

$$\text{Hydrochloric acid} + \text{Zinc} \longrightarrow \text{Hydrogen} + \text{Zinc chloride}$$
$$2\,HCl + Zn \longrightarrow H_2 + ZnCl_2$$

$$\text{Phosphoric acid} + \text{Zinc} \longrightarrow \text{Hydrogen} + \text{Zinc phosphate}$$
$$2\,H_3PO_4 + 3\,Zn \longrightarrow 3\,H_2 + Zn_3(PO_4)_2$$

These reactions are after the manner of reactions that can be expected to result from all contacts between *acids and metals above hydrogen*, with hydrogen substance and salts as products:

Acid + Metal (above hydrogen) → Hydrogen + Salt

Thus, when aluminium, chromium, or iron is in contact with the above acids or with other acids one can expect to obtain hydrogen and aluminium salts, chromium salts, or ferrous salts respectively.

Speed of reaction varies with activity of acid. The speed with which hydrogen and the salt are made from such a reaction depends, as with all reactions, on several factors, area of contact between the acid and metal being one of them (p. 22). But the activity of

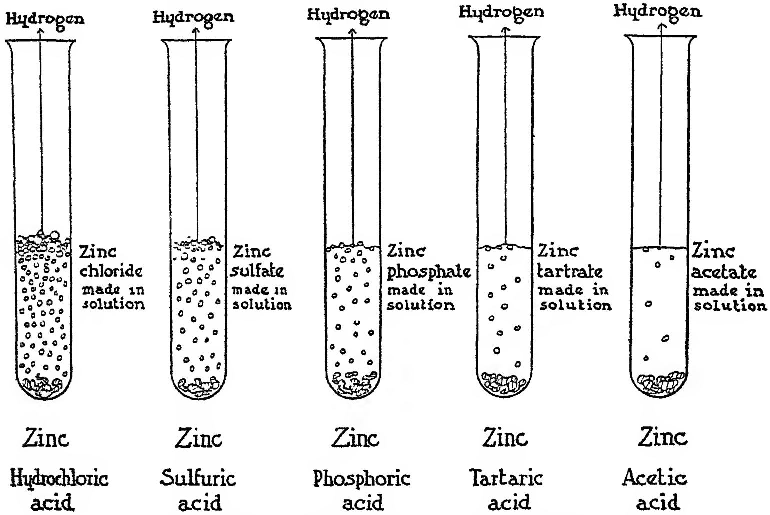


FIG. 55. The Same Metal in Reaction with Different Acids

the acid — the chemist says the *strength of the acid* — is another important reaction speed factor. For example: in the series of contacts specified in Figure 55, if approximately the same surface of contact is presented by the same metal, in this case zinc, and if the several acids are of the same normality (meaning that solutions of acids are such that their hydrogen radicals are of the same concentration, p. 228), the comparative speeds of reactions will be as follows:

Greatest between the zinc and hydrochloric acid,
Somewhat less speedy between zinc and sulfuric acid,
Appreciably less speedy between the zinc and phosphoric acid,
Considerably less so between the zinc and tartaric acid,
Very slow, but still appreciable, between zinc and acetic acid.

These differing reaction speeds, therefore, are entirely due to the *differing activities of the acids* used, hydrochloric acid being the most active and acetic acid the least active of this specific selection of acids.

Varies with activity of metal. On the other hand, if a series of *different metal substances* is in contact with the *same acid* of the

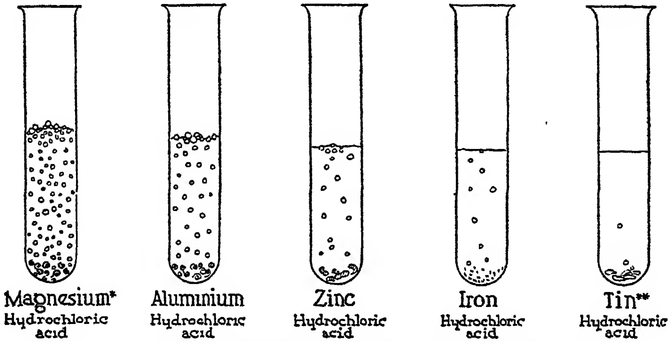


FIG. 56. Different Metals in Reaction with the Same Acid

* Caution is necessary since this reaction is violent.
** Hydrogen is made so slowly as not to be evident to the eye.

same solution normality, it will be found that the speed with which hydrogen and the salt are made will depend upon the *activity of the metal* (Fig. 56).

Obviously, these differing tendencies of various acids and of various metals to engage in reactions is of great significance in practical concerns. This subject will receive consideration later.

Acids with metals below hydrogen. From contacts between acids and metals *below* hydrogen, although salts are made when reactions do occur, no hydrogen product can, in general, be expected; there are two or three exceptions which will receive mention presently. Also, there are differences as to reaction possibility and products from contacts of these metals with acids which *do not* contain oxygen or *binary acids*, and with acids which *do* contain oxygen or *ternary acids*. We shall consider such contacts separately.

Binary acids with metals below hydrogen. The four acids of consequence of this variety are:

Hydrochloric acid............	$H\ Cl$
Hydrobromic acid............	$H\ Br$
Hydroiodic acid............	$H\ I$
Hydrosulfuric acid...........	H_2S

And, in general, *no reaction* can be expected to follow from contacts between any of these acids and metals below hydrogen:

Acids (without oxygen) + Metals (below hydrogen) → No reaction

Hydrochloric acid + Copper → No reaction
Hydrochloric acid + Silver → No reaction
Hydrochloric acid + Platinum → No reaction

Exceptions. Exceptions to this rule are in respect to the binary acid *hydrosulfuric acid* and the metals *copper*, *mercury*, and *silver* which do engage in reactions to make hydrogen and salts. Thus:

Hydrosulfuric acid + Copper → Copper sulfide + Hydrogen

$$H_2S + Cu \longrightarrow CuS + H_2$$

Hydrosulfuric acid + Silver → Silver sulfide + Hydrogen

$$H_2S + 2\,Ag \longrightarrow Ag_2S + H_2$$

Indeed, it is when hydrogen sulfide gets into the air from various sources, such as from so-called sulfur springs and from the burning of soft coal, that silverware becomes tarnished or covered with a layer of black silver sulfide.

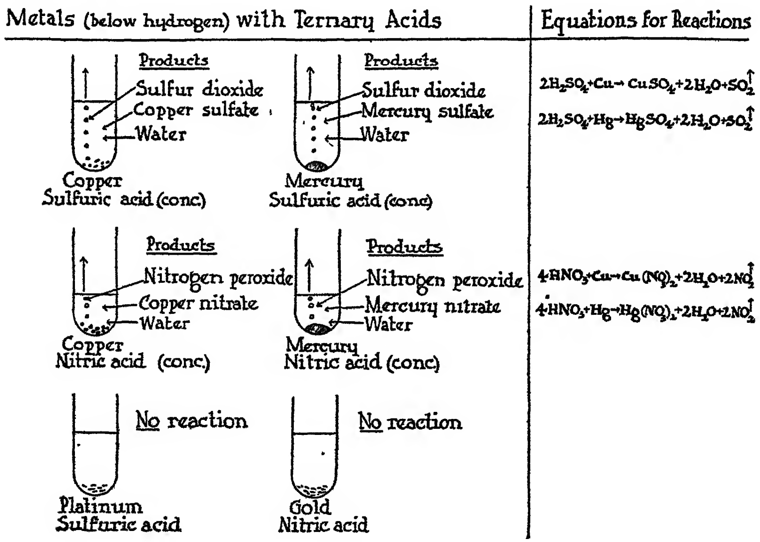


FIG. 57

Ternary acids with metals below hydrogen. Selected contacts of ternary acids with metals below hydrogen are presented above and the products of reactions are as specified (Figure 57).

And these reactions exemplify reactions that one can expect to take place from contacts between other oxygen-containing

acids with copper, mercury, and silver to make salts of the respective metals, water, and other substances. But from contacts between such acids and platinum or gold no reactions whatsoever take place even at very high temperatures:

Acid (containing oxygen) +	Copper Mercury Silver	→ Salt + Water +	Some other substance

Acid (containing oxygen) + Platinum → No reaction

Reactions as to acids and metals in practical concerns. Since gold is soft, platinum, which is almost as inactive as gold, would be the ideal metal for uses for which metal substances are employed. Household utensils, laboratory apparatus, drainage and water pipes made of platinum would be most desirable, if only this metal were less costly. Consequently, platinum not being practical, selections from other metal substances must be made for the manufacture of utensils and other containers, metal plates, wires, etc., depending upon the cost of the metal substances and the uses to be made of these utilities.

In laboratories. Hydrochloric acid, sulfuric acid, and nitric acid are three reagents that are employed extensively in laboratory practice. Therefore, pieces of apparatus which are to be used in contact with these acids are never of aluminium, or zinc, or iron, or copper, since all of these acids, as well as others of occasional use, would react appreciably with aluminium, zinc, or iron containers, or with containers of any other metals above hydrogen, while sulfuric and nitric acids would also react with copper containers. Accordingly, laboratory apparatus that is to encounter acid reagents is commonly made, not of metals, but of glass or porcelain.

In cookery concerns. Metal containers are indeed used in cookery, but the acid components of food — tartaric, citric, lactic, and acetic acids among them — are all *weak* acids, hence with any save the most active metals, reactions are from very slow to inappreciable.

Metal containers of ancient use were of iron and of copper. These are still used, but so are utensils of aluminium and nickel. With aluminium utensils the weak acids of food mixtures react only slowly, even at the high temperatures maintained for food preparations; as for iron utsensils, reactions with food acids are even slower, although in long contacts, especially at high temperatures, appreciable reactions do occur; with nickel utensils reactions

are from extremely slow to inappreciable. Products of these reactions are, as should be expected, hydrogen and salts of the metals and food acids involved — aluminium tartrate, aluminium citrate, iron tartrate, iron citrate, etc.

Copper utensils are not widely used today in food preparations. However, since all food acids are oxygen-containing acids, if these are kept in contact with copper, especially at the high temperatures obtained in cooking, a limited amount of reaction would undoubtedly take place, while copper salts of the acids together with other substances would be made as products.

Are the salts injurious? Aside from the cost factor and that of a reaction possibility with food acids, another item in the selection of a metal for the making of cooking utensils that must receive consideration is that of whether any salt products, which of necessity get mixed with the food mass, have any undesirable physiological effects. It is for this reason that neither zinc nor lead is advisable for cooking utensils since both would react with food acids, the former to make zinc salts which are irritating, the latter to make lead salts which are poisonous. As for such quantities of aluminium salts as are ingested along with the food cooked in aluminium utensils, there is no authoritative evidence that they are physiologically harmful. It seems certain that the iron salts of such origin that get absorbed are not harmful; they may even be desirable.

Acids with metal oxides. When an acid and a metal oxide are placed in contact with each other a reaction sets in from which the products are water and a salt, the salt containing the metal element, previously within the metal oxide, and the acid radical, previously within the acid:

$$\text{Acid} + \text{Metal oxide} \rightarrow \text{Water} + \text{Salt}$$

Reactions from some such contacts take place quite rapidly; from other contacts they take place from slowly to inappreciably. For example:

When solutions of hydrochloric acid and nitric acid are in contact with ferric oxide and copper oxide (Fig. 58), reactions very soon begin to be apparent, as evidenced by the appearance of yellowish brown ferric chloride from the first reaction, and blue cupric nitrate from the second reaction. If the acids are weak, such as tartaric, lactic, and acetic acids, reactions with metal oxides are, of course, much slower than with the aforementioned strong acids.

But that reactions of metal oxides even with weak acids do

become appreciable in time is evidenced by the fact that when grapes which contain tartaric acid, or tomatoes which contain citric acid, are heated in a dull aluminium kettle, or when sour milk is set away in such a tarnished aluminium dish, the dull coating of metal

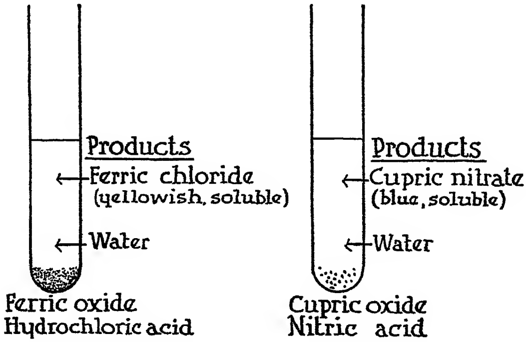


FIG. 58. Acids React with Metal Oxides

rust disappears. The reason is that this coating is aluminium oxide; consequently, as should be expected, weak acids react slowly but surely with this oxide to make water and aluminium tartrate, aluminium citrate, or aluminium lactate, respectively:

$$\begin{array}{ccccccc} \text{Tartaric acid} & + & \text{Aluminium oxide} & \rightarrow & \text{Water} & + & \text{Aluminium tartrate} \\ 3\,H_2C_4H_4O_6 & + & Al_2O_3 & \longrightarrow & 3\,H_2O & + & Al_2(C_4H_4O_6)_3 \end{array}$$

$$\begin{array}{ccccccc} \text{Citric acid} & + & \text{Aluminium oxide} & \rightarrow & \text{Water} & + & \text{Aluminium citrate} \\ 2\,H_3C_6H_5O_7 & + & Al_2O_3 & \longrightarrow & 3\,H_2O & + & 2\,AlC_6H_5O_7 \end{array}$$

These salts, being more or less soluble, get mixed with the grapes, the tomatoes, or the sour milk. Similar reactions remove iron rust, or ferric oxide, from rusted iron utensils, with water and the ferric salts of the acids concerned appearing as products.

Chemical reactions that take place between ***acids and bases*** and between ***acids and salts*** will be presented later (pp. 200–201).

BASES WITH METALS

In review. Before continuing with the study of bases, the composition of bases should be reviewed, also representative bases, and the effect produced by bases in water solution on red litmus (pp. 131–133).

Bases in reaction with metals. There is considerable limitation in regard to what to expect by way of reactions from bases with metals, since, in the main, reactions take place only from contacts between the two bases, potassium hydroxide and sodium hydroxide,

and the three metals, aluminium, zinc, and tin. The products of these reactions are hydrogen and salts — aluminates, zincates, and stannates:

Sodium hydroxide +	Aluminium ⟶	Hydrogen +	Sodium or Potassium
Potassium hydroxide	Zinc		aluminate
	Tin		zincate
			stannate

Reactions between sodium hydroxide and these metals are illustrated and described in Figure 59:

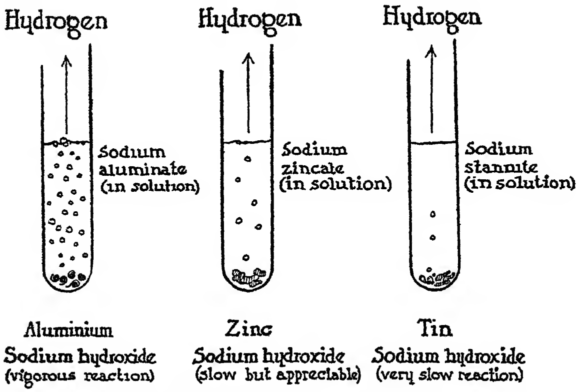


FIG. 59. Certain Bases React with Aluminium, Zinc, and Tin

Sodium hydroxide + Aluminium ⟶ Hydrogen + Sodium aluminate[1]

$$6\,NaOH + 2\,Al \longrightarrow 3\,H_2 + 2\,Na_3AlO_3$$

Potassium hydroxide of like solution concentration with these metals give like results, save that the salts made are potassium salts.

Practical applications. Whenever chemists are in charge of operations, contacts between these two bases and metal substances are carefully avoided unless reaction is desired. But in *housekeeping practices* contacts between sodium hydroxide and these metals are of more or less frequent occurrence. The following are examples:

1. Any commercial lye is quite likely to be over 90 per cent *sodium hydroxide.* Whenever a solution of such a lye is used for cleaning out a drain with iron or lead pipe connections, no reaction between the sodium hydroxide and either of these metals will take place. But if used for cleaning aluminium utensils, or galvanized iron (iron covered with layers of zinc) pails or tubs, reaction most certainly occurs, more with aluminium than with zinc. If,

[1] Some claim that reaction as represented in the following equation takes place between aluminium and these bases:

$$2\,Al + 2\,NaOH + 2\,H_2O \rightarrow 3\,H_2 + 2\,NaAlO_2$$

therefore, such lye is used at all for the cleansing of aluminium or zinc utensils it should be in *exceedingly* dilute solution, and should not be permitted to stand in contact with either metal for any length of time.

This is probably the only direct source of this strong base that is encountered in household practice. Potassium hydroxide is not met with at all.

2. But sodium carbonate is used quite generally in housekeeping, either under the label of washing soda, or as an unmentioned component of "magical" cleaning agents under their commercial labels. Sodium carbonate is obviously not a base in itself, but when in water solution some of it reacts with water to make *sodium hydroxide*, not in high concentration to be sure (p. 180), but in sufficient concentration to react slowly with aluminium and zinc. Hence, whenever washing soda solution is permitted to stand in aluminium utensils, or in galvanized iron pails and tubs, slow reaction does take place, not due to washing soda, but due to the dilute solution of sodium hydroxide that is made.

$$Na_2CO_3 + 2\,HOH \rightarrow 2\,NaOH + H_2CO_3$$

Reactions that take place from contacts between ***bases and acids*** and between ***bases and salts*** will be studied later in this chapter.

SALTS WITH METALS

In review. As with the studies of acids and bases, before continuing with the further study of salts, it would be well to review the composition of salts (p. 136) and make a list of typical salts.

Salts in reaction with metals. Whether a salt in solution will or will not react with a metal substance depends on whether the metal element within the metal substance is more active or less active than the metal element within the salt. Thus:

Sodium chloride + Zinc ⟶ No reaction	Magnesium sulfate + Iron ⟶ No reaction
↑	↑
less active than	less active than
↑	↑
ZINC (element)	IRON (element)
↓	↓
more active than	more active than
↓	↓
Lead nitrate + Zinc → Lead + Zinc nitrate	Copper sulfate + Iron → Copper + Iron sulfate

More detailed reasoning is as follows:

Zinc (substance) contains zinc element which displaces the less active lead from the salt	+	Lead nitrate	⟶	Lead (substance) built of the less active lead element	+	Zinc nitrate in which the more active zinc element gains the acid radical partner.

A brief general statement, then, in regard to the reaction that can be expected to follow from a salt and metal contact would be as follows:

Salt + Metal (substance containing a more active metal element) ⟶ Salt (of more active metal) + Metal (substance containing a less active metal element)

Some practical consequences. *In the laboratory.* Herein lies another reason why apparatus made of glass or porcelain is advisable for general use rather than of some metals. Aluminium beakers, bottles, etc., could reasonably be used to hold solutions of magnesium, calcium, sodium, or potassium salts without any reaction taking place between the substance aluminium and said salts. (Why?) But should the salts contain zinc, chromium, iron, or any of the metal elements less active than aluminium, reaction between any of these salts and aluminium (substance) of the container would set in. Or if the apparatus were made of chromium or of nickel, while reaction would *not* take place between either of these substances and salts containing metal elements more active than the elements chromium or nickel; with salts of metals below chromium or nickel reactions *would* occur, and all such salts are used in laboratory experimental work.

In housekeeping concerns, the salts and metal substances that are more or less commonly encountered are as follows:

The salts	*Metals*
Potassium chloride, Sodium chloride, Calcium chloride, Magnesium chloride } components of meats and vegetables	Aluminium (of containers, spoons, etc.)
Iron salts (components of such foods as beans, eggs, oatmeal, oysters, spinach)	Zinc (of garbage pails, and tubs)
	Iron (cooking utensils)
	Nickel (utensils in institutional cookery)
	Silver (of cutlery)

Hence, a study of the activity placement of metal elements in respect to each other (p. 172) will reveal the following facts. When foods containing potassium, sodium, calcium, and magnesium salts are cooked in containers made of any of the above metal substances, likewise when silverware is used in handling these foods, no reaction occurs as far as the salts and metals are concerned. When foods containing iron salts are cooked in aluminium utensils, some reaction can be expected to set in between said salts and the aluminium, but not so if these foods are cooked in containers of the other metal substances specified:

Sodium salt + Aluminium → No reaction
Magnesium salt + Aluminium → No reaction
Iron salt + Aluminium → Iron + Aluminium salt
Iron salt + Nickel → No reaction

In hospital practice, aside from salt and metal contacts which are encountered in food preparations and handling as stressed above, other such contacts are as follows:

Salts	*Metals*
Potassium permanganate (for irrigations)	Chromium (plated instruments, table tops, etc.)
Sodium chloride } for dressings and	Nickel (plated instruments, etc.)
Magnesium sulfate } packs	
Mercuric chloride (for dressings)	
Silver nitrate (for irrigations)	

Evidently, sodium chloride and magnesium sulfate dressings and packs can be handled with chromium or nickel-plated instruments without any reaction between these salts and these metal substances taking place. But mercuric chloride dressings should be handled very speedily, if at all, with such instruments; and by no means should forceps or other instruments of these metals be permitted to stand in the mercury salt solution. The same caution holds in respect to silver nitrate solution, since, like mercury salts, silver salts in solution do react with both chromium and nickel:

Magnesium sulfate + Nickel → No reaction
Mercuric chloride + Nickel → Mercury + Nickel chloride
Silver nitrate + Chromium → Silver + Chromium nitrate

Reactions that take place between (1) ***salts and water*** in direct combination ***to make hydrates*** (p. 177), and between (2) ***salts and water*** in hydrolysis ***to make acids and bases*** (p. 180) have been presented previously and should be reviewed at this time.

ACIDS, BASES, AND SALTS IN REACTION WITH EACH OTHER

There are such marked similarities in reactions among acids, bases, and salts as to each other, that it seems logical to make these studies in one section.

Acid and base. When solutions of an acid and a base are brought into contact a reaction takes place in which water and a salt are made, the latter containing the metal radical of the base and the acid radical of the acid:

Acid + Base → Water + Salt

An experiment commonly performed and one that makes this sort of reaction clearer to the student, because of familiarity with the salt product, is as follows:

Make very dilute solutions of hydrochloric acid and of sodium hydroxide. Put about half of the acid solution into an evaporating dish and add to this the base solution, first a little at a time and later drop by drop. After each addition of the base solution, stir thoroughly and transfer a drop of the solution to a strip of blue litmus paper on a watch glass to see if the acid still predominates over the base (Fig. 60). When no effect is produced with the blue litmus, transfer a drop of the solution to the red litmus paper to see if the base predominates. Since the aim is to obtain a solution in which the acid and base have completely neutralized each other, from then on, the acid or the base solution — depending on the effect with litmus — should be added until no effect is produced with either the red or the blue litmus.

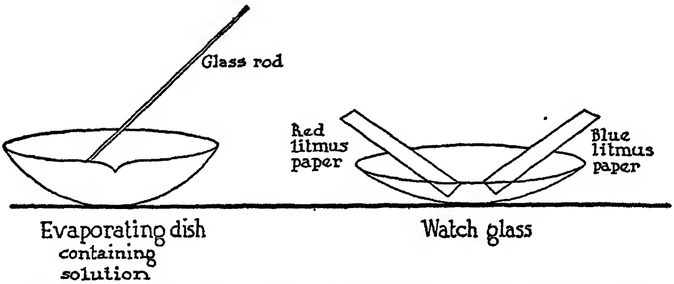


FIG. 60. An Acid with a Base, Testing for the Neutral End Point

When this end point has been reached, evaporate the water, heating the solution to increase the speed of evaporation. Eventually, a white solid, previously in solution, will appear, which upon testing will taste like sodium chloride, and rightly so since it is sodium chloride. The water product has been evaporated along with the extra water used for solution purpose:

$$\text{Hydrochloric acid} + \text{Sodium hydroxide} \longrightarrow \text{Water} + \text{Sodium chloride}$$
$$HCl + NaOH \longrightarrow H_2O + NaCl$$

Exactly the same procedure can be followed in gathering evidence of the making of other soluble salts as, for example, in the making of potassium sulfate from the reaction of sulfuric acid with potassium hydroxide, and the making of sodium tartrate from the reaction of tartaric acid with sodium hydroxide:

$$\text{Sulfuric acid} + \text{Potassium hydroxide} \longrightarrow \text{Water} + \text{Potassium sulfate}$$
$$H_2SO_4 + 2\,KOH \longrightarrow 2\,H_2O + K_2SO_4$$

If the salt product is insoluble, it gives evidence of its making almost immediately upon bringing the acid and base together, because of its automatic precipitation. Thus:

When solutions of sulfuric acid and calcium hydroxide are put into contact, almost immediately a white insoluble substance appears which is calcium sulfate and, of course, water is made along with it (Fig. 61):

$$\text{Sulfuric acid} + \text{Calcium hydroxide} \rightarrow \text{Water} + \text{Calcium sulfate}$$
$$H_2SO_4 + Ca(OH)_2 \longrightarrow H_2O + CaSO_4$$

The reverse of hydrolysis. This reaction of an acid with a base is, as should be noted, the reverse of that reaction in which a smaller or larger portion of a salt reacts with water in double decomposition, or hydrolysis, to make an acid and a base (p. 180):

Base + Acid ⇄ Water + Salt

This means that no sooner have a base and an acid reacted to make water and a salt, than some of the salt product (if soluble) begins to react with the water to remake portions of the acid and base. The extent of the reverse reaction accomplished depends on various factors, two of which are: (1) the strength, meaning chemical activity, of the acid and base, and (2) whether the water and salt are kept in contact. For example:

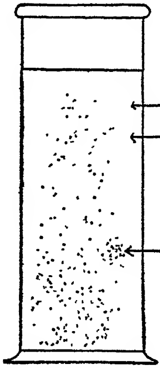


FIG. 61. An Acid with a Base, an Insoluble Salt as a Product

1. Sodium hydroxide is such a very active (strong) base and hydrochloric acid such a very active (strong) acid that, when they are brought together in solution, reaction is carried almost to completion toward the making of water and sodium chloride. It follows, then, that when the two reactions attain equilibrium, concentrations of the water and sodium chloride products are relatively high, while those of the beginning substances, sodium hydroxide and hydrochloric acid, are very low.

Sodium hydroxide + Hydrochloric acid ⇄ Water + Sodium chloride

But should the water be continuously removed by evaporation, as was the case in the experiment described on page 198, reaction is then carried entirely to completion in the direction of the making of water and salt products:

Sodium hydroxide + Hydrochloric acid → Water + Sodium chloride

2. When calcium hydroxide and sulfuric acid are the base and acid used, there are two reasons why reaction is carried almost to completion in the direction of making water and calcium sulfate (Fig. 61). 1st, the base and acid are both chemically active or strong; 2nd, the salt product is not very soluble so that most of it is removed from contact with the water almost as rapidly as it is made:

Calcium hydroxide + Sulfuric acid ⇄ Water + Calcium sulfate ↑↓

Note. — Double arrows are used to indicate either the existence or the possibility of two opposing reactions taking place at the same time. When so desired, relative concentrations of beginning substances and products are

represented either by a difference in thickness or a difference in length of the two arrows — the longer or heavier arrow pointing toward substances in higher concentration, the shorter or lighter arrow pointing toward substances in lower concentration.

Removal of a substance by evaporation or of an insoluble gaseous substance is indicated by an upward-pointing arrow; removal of a substance by precipitation is indicated by a downward-pointing arrow.

Reactions between acids and bases in practical concerns. *Industrially*, one of the methods for making salts is from reactions between acids and bases. And, other conditions being favorable, an excellent method it is, since the salt can be so easily made at the expense of the acid and base, and separated at the same time from contact with the associated product, water, by merely evaporating the latter.

Stain removal. In such reactions lie the best possible means for removing acid and base stains on fabrics. If the stain is caused by a base, then a solution of a weak acid, such as acetic acid, used carefully may remove it; if the stain is caused by an acid, then a solution of a weak base, such as ammonium hydroxide, may remove it.

To prevent acid poisoning. And herein lies the reason why a base, given as quickly as possible, is prescribed as an antidote for acid poisoning. For this purpose calcium hydroxide, a component of lime water, or magnesium hydroxide, a component of milk of magnesia, is commonly advised. If, for example, the acid taken is oxalic acid, it is destroyed by the calcium hydroxide or magnesium hydroxide to make water and calcium oxalate or magnesium oxalate; furthermore, the insolubility of calcium and magnesium oxalates insures the carrying of both of these reactions to completion in the direction of the making of these salts, hence the complete removal of the oxalic acid. If the acid is hydrochloric acid, which has been taken beyond the limits of safety, then the excess can be destroyed by giving an advised dosage of one or the other of these two bases, to make water and calcium chloride or magnesium chloride.

$$\begin{array}{ccccccc} \text{Oxalic acid} & + & \text{Calcium hydroxide} & \rightarrow & \text{Water} & + & \text{Calcium oxalate} \\ H_2C_2O_4 & + & Ca(OH)_2 & \longrightarrow & 2\,H_2O & + & CaC_2O_4\downarrow \end{array}$$

$$\begin{array}{ccccccc} \text{Hydrochloric acid} & + & \text{Magnesium hydroxide} & \rightarrow & \text{Water} & + & \text{Magnesium chloride} \\ 2\,HCl & + & Mg(OH)_2 & \rightarrow & 2\,H_2O & + & MgCl_2 \end{array}$$

Against accidents with a strong base, an acid, administered speedily, is the antidote. For such purpose acetic acid, the acid component of vinegar, or the weak acids of lemon juice is usually advised.

Physiologically. Reactions of this sort that take place in the body constitute one of nature's devices for preventing the various acids and bases present within the cells, lymph, and blood from ever piling up in any considerable quantities. Hydrochloric acid, sodium hydroxide, potassium hydroxide, as well as other acids and bases, are always present in the body fluids; carbonic acid, phosphoric acid, sulfuric acid, and ammonium hydroxide are made in the cells as products of various metabolic reactions. But none of these acids or bases can acquire a high concentration, because they all engage in various reactions, among them these base and acid reactions to make water and salt products.

Acid and salt. When an acid and a salt, which contain different acid radicals, are together in water solution, another acid and another salt are made. Such a reaction takes place between sulfuric acid and sodium nitrate.

$$\textbf{Acid} + \textbf{Salt} \rightleftarrows \textbf{Acid} + \textbf{Salt}$$
$$\text{Sulfuric acid} + \text{Sodium nitrate} \rightleftarrows \text{Nitric acid} + \text{Sodium sulfate}$$
$$H_2SO_4 + 2\,NaNO_3 \rightleftarrows 2\,HNO_3 + Na_2SO_4$$

Base and salt. When solutions of a base and a salt which contain different metal radicals are placed together, another base and another salt are made. One such reaction takes place between calcium hydroxide and ammonium chloride:

$$\textbf{Base} + \textbf{Salt} \rightleftarrows \textbf{Base} + \textbf{Salt}$$
$$\text{Calcium hydroxide} + \text{Ammonium chloride} \rightleftarrows \text{Ammonium hydroxide} + \text{Calcium chloride}$$
$$Ca(OH)_2 + 2\,NH_4Cl \rightleftarrows 2\,NH_4OH + CaCl_2$$

Salt and salt. When a salt and a salt, which contain different metal radicals and different acid radicals, are in contact with each other in water solution, a reaction sets in during which two different salts are made. One of the many reactions between two salts, and one which is of considerable importance commercially, is that between sodium nitrate and potassium chloride to make the desired potassium nitrate, which is so necessary as a fertilizer and in the manufacture of explosives:

$$\textbf{Salt} + \textbf{Salt} \rightleftarrows \textbf{Salt} + \textbf{Salt}$$
$$\text{Sodium nitrate} + \text{Potassium chloride} \rightleftarrows \text{Potassium nitrate} + \text{Sodium chloride}$$
$$NaNO_3 + KCl \rightleftarrows KNO_3 + NaCl$$

Reversible reactions. Reactions from all four contacts of the foregoing discussion as to acids, bases, and salts are reversible.

Therefore, in every instance in which the *products are kept in contact with each other* they react to a greater or less extent to remake portions of the initial compounds. It follows, then, that within such a solution *four compounds are present* and *two opposing reactions* are taking place with an aim toward establishing an equality of reaction speed, or a condition of equilibrium (Fig. 62 A).

How carry the forward reaction to completion? However, if one of the products is continuously removed, the forward reaction is continuously favored until the beginning compounds are either almost or else completely gone. Such a removal occurs if one of

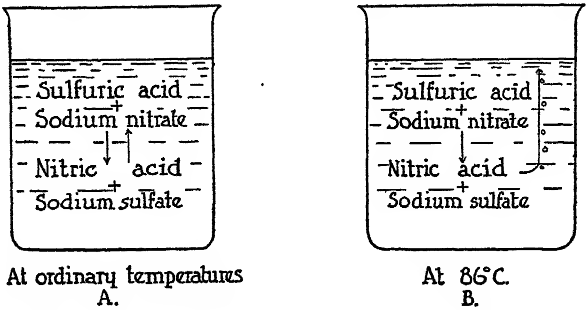


FIG. 62. An Otherwise Reversible Reaction (A) Carried to Completion through the Removal of One of the Products (B)

the products: (1) is evaporated (examples: p. 198, also Fig. 62 B); (2) is a slightly insoluble gas (Fig. 63); (3) is precipitated because of its slight solubility (Fig. 61); (4) engages in another reaction almost as rapidly as it is made (p. 203). Thus:

1. From reaction between sulfuric acid and sodium nitrate, the products are nitric acid and sodium sulfate; and since, at ordinary temperatures, these products are both soluble, they are automatically kept in contact and the reverse reaction sets in to make the initial compounds. Hence, two reactions get into operation and portions of all four compounds are present (Fig. 62 A):

$$H_2SO_4 + 2\ NaNO_3 \rightleftharpoons 2\ HNO_3 + Na_2SO_4$$

But if the temperature of the solution is raised to 86° C., the boiling point of nitric acid, this compound vaporizes and is thereby continuously removed (Fig. 62 B). This results in a continuous favoring of the reaction in the direction of the making of more nitric acid and sodium sulfate until both of the beginning compounds are gone, provided there were just the right proportions of sulfuric acid and sodium nitrate to *exactly* react with each other, and only sodium sulfate remains in the dish:

$$H_2SO_4 + 2\ NaNO_3 \longrightarrow 2\ HNO_3\uparrow + Na_2SO_4$$

An acid and a carbonate salt. When an acid and a salt that contains the carbonate radical are in contact with each other the acid product must always be carbonic acid. But carbonic acid is (1) only slightly soluble and (2) it is unstable; as a result, most of this acid decomposes as rapidly as it is made and the products are carbon dioxide and water. However, carbon dioxide also is only slightly soluble, therefore, almost as rapidly as it is made, it bubbles out of the solution. The result is that, due to this removal of carbonic acid and carbon dioxide, in turn, reaction between any acid and any carbonate, at ordinary temperatures, is carried almost to completion in the direction of the making of the salt product:

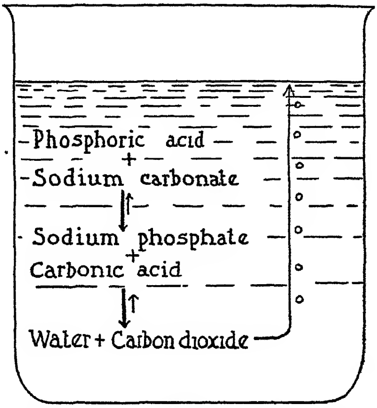


FIG. 63. An Acid with a Carbonate

$$\text{Acid} + \text{Carbonate} \rightleftarrows \text{Carbonic acid} + \text{Salt}$$
$$\uparrow\downarrow$$
$$\downarrow\uparrow\ \text{Carbon dioxide} + \text{Water}$$

For example: If the acid is phosphoric acid and the salt is sodium carbonate, at ordinary temperatures most of the carbonic acid and most of the carbon dioxide are removed from the solution. As a result, when the two reactions as to the acids and salts attain equilibrium, the concentration of the initial phosphoric acid and sodium carbonate will be very low, while that of sodium phosphate product will be high:

$$2\,H_3PO_4 + 3\,Na_2CO_3 \rightleftarrows 3\,H_2CO_3 + 2\,Na_3PO_4$$
$$\uparrow\downarrow$$
$$3\,H_2O + 3\,CO_2 \uparrow\downarrow$$

But if the temperature of the solution is raised, the instability of carbonic acid is increased and carbon dioxide is rendered insoluble. Consequently, under these conditions reaction in the forward direction will eventually be carried entirely to completion with *only* sodium phosphate left in solution (Fig. 63):

$$2\,H_3PO_4 + 3\,Na_2CO_3 \longrightarrow 3\,H_2CO_3 + 2\,Na_3PO_4$$
$$\downarrow$$
$$3\,H_2O + 3\,CO_2 \uparrow$$

Practical importance of reactions:

Acid + Salt ⇄ Acid + Salt
Acid + Carbonate ⇄ Carbonic acid + Salt
Base + Salt ⇄ Base + Salt
Salt + Salt ⇄ Salt + Salt

In the laboratory and commercially the first of these contacts serves as one means for *making acids;* the third as one means for *making bases;* all serve as possibilities for *making salts.* Of course, whether any of these contacts is selected for the making of this or that acid, or base, or salt must depend upon various considerations including: (1) whether a reasonable selection of initial substances can be obtained and (2) whether properties of the products are such that conditions can be brought to bear which will permit of carrying the reaction to completion in the direction of the making of the desired acid, or base, or salt.

Hard water and its softening. Hard water is water which contains certain soluble salts, usually soluble calcium or magnesium salts, or both. *Soap* is a mixture of the salts sodium stearate, sodium palmitate, and sodium oleate (p. 339):

Salts of hard water		*Salts of hard soaps*	
Calcium chloride......	$CaCl_2$	Sodium stearate.....	$NaC_{17}H_{35}CO_2$
Calcium sulfate........	$CaSO_4$	Sodium palmitate....	$NaC_{15}H_{31}CO_2$
Calcium hydrogen carbonate............	$Ca(HCO_3)_2$	Sodium oleate.......	$NaC_{17}H_{33}CO_2$
Corresponding magnesium salts			

Accordingly, when soaps are rubbed into hard water their salts react with the salts of hard water and are destroyed, thereby preventing them from performing their cleansing service. Moreover, the calcium (or magnesium) stearate, palmitate, and oleate made are insoluble — they form the familiar flaky precipitate which collects on the sides of the bowl or pan when one uses soaps with hard water; therefore, reactions in the forward direction are continuously favored, and the soap is continuously destroyed, until such time as no more of the salts of hard water remain:

Calcium chloride (of hard water) + Sodium stearate (of soap) → Calcium stearate ↓ + Sodium chloride

$$CaCl_2 + 2\,NaC_{17}H_{35}CO_2 \rightarrow Ca(C_{17}H_{35}CO_2)_2\downarrow + 2\,NaCl$$

Softening of hard water calls for the introduction of some compound, such as sodium carbonate, before the soap is rubbed in, which will react with the salts of hard water to make insoluble

calcium or magnesium salts, thereby removing the offending calcium or magnesium radical from solution. And so, again, we meet with a reaction between two salts to make two other salts, one of the latter being insoluble. Two such reactions are represented as follows:

$$\underset{\substack{\text{(one soluble salt}\\ \text{of hard water)}}}{\substack{\text{Calcium}\\ \text{chloride}}} + \substack{\text{Sodium}\\ \text{carbonate}} \longrightarrow \substack{\text{Calcium}\\ \text{carbonate}\downarrow} + \substack{\text{Sodium}\\ \text{chloride}}$$

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2\,NaCl$$

$$\underset{\substack{\text{(one soluble salt of}\\ \text{hard water)}}}{\substack{\text{Calcium hydrogen}\\ \text{carbonate}}} + \substack{\text{Sodium}\\ \text{carbonate}} \longrightarrow \substack{\text{Calcium}\\ \text{carbonate}\downarrow} + \substack{\text{Sodium hydrogen}\\ \text{carbonate}}$$

$$Ca(HCO_3)_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2\,NaHCO_3$$

In cookery. When sour milk and baking soda are mixed in cookery procedures, the reactions which are responsible *first*, for the fizzing and *second*, for "lifting" of the cake or biscuit dough in the hot oven, are according to the reactions which can be expected to follow from contact between any *acid* and salt which is a *carbonate* (p. 203). The sour milk contains lactic acid, baking soda is sodium bicarbonate, the acid product is carbonic acid which, being unstable, decomposes to make water and carbon dioxide, hence the initial fizzing. At ordinary temperatures when the effervescence is ended some carbonic acid is still left in the dough mixture:

$$\text{Lactic acid} + \text{Sodium bicarbonate} \rightleftarrows \text{Carbonic acid} + \text{Sodium lactate}$$

$$\begin{array}{ccccccc} HC_3H_5O_3 & + & NaHCO_3 & \rightleftarrows & H_2CO_3 & + & NaC_3H_5O_3 \\ & & & & \uparrow\downarrow & & \\ & & & & H_2O + CO_2 \updownarrow & & \end{array}$$

But when the biscuits or cakes are put into the oven, the eventual high temperature obtained within the dough mass favors decomposition of the remaining carbonic acid; and the escape of the carbon dioxide made "lifts" or aerates the dough mass on its way out. Eventually, providing there is no excess of either lactic acid or sodium bicarbonate, the reaction will be complete with only sodium lactate left in the biscuits. This salt is responsible, in part, for the characteristic flavor of baked foods made with sour milk. The following equation disregards the carbonic acid which is made and promptly destroyed:

$$HC_3H_5O_3 + NaHCO_3 \rightarrow H_2O + CO_2\uparrow + NaC_3H_5O_3$$

In fire extinguishers. In one type of fire extinguisher the desired carbon dioxide is made after this same manner: namely, from *reaction of an acid,* usually sulfuric acid, *with a carbonate,* usually sodium bicarbonate. Within the apparatus is a small bottle of acid and a solution of sodium bicarbonate (Fig. 64). When inverted the acid flows gradually out of the bottle into contact with the carbonate and reaction begins to operate very speedily:

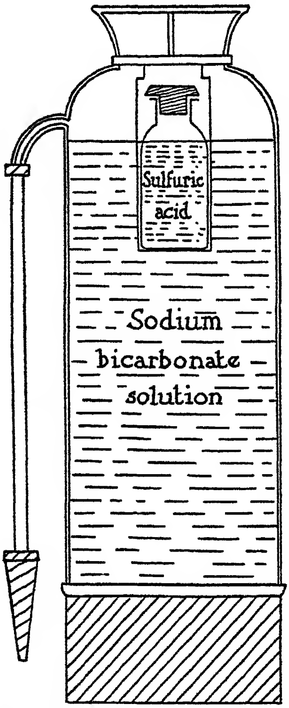


FIG. 64. One Type of Fire Extinguisher

$$
\begin{array}{l}
H_2SO_4 + 2NaHCO_3 \rightleftarrows 2\,H_2CO_3 + Na_2SO_4 \\
\qquad\qquad\qquad\qquad\qquad \downarrow\uparrow \\
\qquad\qquad\qquad\qquad\quad \downarrow\uparrow\ 2\,CO_2 + 2\,H_2O
\end{array}
$$

The stream of solution and of carbon dioxide, ejected forcefully, if well directed, will spread a blanket of nonburnable gases between the partner substances responsible for the burning.

Disinfecting with salts. When either silver nitrate or mercuric chloride (bichloride of mercury) is used as a disinfectant, it kills bacteria because, like all proteins, bacterial proteins are acids (hydrogen proteinates), so the salt disinfectant reacts with these protein acids, as should be expected, to make another acid and other salts. Furthermore, since both silver proteinates and mercuric proteinates are insoluble, the forward reactions, hence the continued destruction of bacterial proteins by the salt, are favored over the reverse reactions. This continues as long as any disinfectant salt is present:

$$
\begin{array}{ccccccc}
\text{Salt} & + & \text{Acid} & \longrightarrow & \text{Salt}\downarrow & + & \text{Acid} \\
\begin{array}{c}\text{Silver}\\ \text{nitrate}\end{array} & + & \begin{array}{c}\text{Hydrogen}\\ \text{proteinate}\end{array} & \longrightarrow & \begin{array}{c}\text{Silver}\\ \text{proteinate}\downarrow\end{array} & + & \begin{array}{c}\text{Hydrogen}\\ \text{nitrate}\end{array} \\
\begin{array}{c}\text{Mercuric}\\ \text{chloride}\end{array} & + & \begin{array}{c}\text{Hydrogen}\\ \text{proteinate}\end{array} & \longrightarrow & \begin{array}{c}\text{Mercuric}\\ \text{proteinate}\downarrow\end{array} & + & \begin{array}{c}\text{Hydrogen}\\ \text{chloride}\end{array}
\end{array}
$$

Reactions with antidotes. The above reaction of silver nitrate on proteins is as fatal to proteins of human tissue cells as to those of bacteria. For this reason silver nitrate — or any soluble silver

salt — is a poison, the prescribed antidote for which is a solution of sodium chloride to be applied plentifully and speedily in order to destroy the silver nitrate before it has time to enter the cells. Sodium chloride can function thus because it reacts with silver nitrate to make silver chloride which is only very slightly soluble; as a result, very little, if any, silver chloride product, precipitated thus outside of the cells, can pass through cell membranes to attack proteins therein.

$$AgNO_3 + NaCl \rightarrow AgCl \downarrow + NaNO_3$$

One example of the use of sodium chloride thus as an antidote for silver nitrate is as follows. It is customary to inject silver nitrate (1 per cent) into the eyes of newborn infants, as a prophylactic measure to destroy any gonococci which might possibly be present. Then, this injection is frequently followed by an irrigation of "physiological salt solution" (8.5 grams of sodium chloride in 1 liter of solution) so that the sodium chloride will, in turn, destroy any *remaining* silver nitrate, thereby preventing any serious attack by this salt on the tissue cells themselves.

This is but one of a number of soluble salts and acids, which are poisonous, for each of which some particular salt, or acid, or base functions as an antidote by precipitating within an insoluble compound the offending radical, thus rendering it incapable of passing through cell membranes.

Physiologically. Various acids, bases, and salts are distributed in the blood, lymph, and cells within the body. Some are absorbed, as such, directly from the food mixtures obtained in the intestine; some are made within the cells and enter the lymph and blood from that source (p. 455). And, as has been pointed out previously, proteins are acids, so also are amino acids from which they are made. However, regardless of the source of these compounds, the fact remains that wherever within the body an *acid and a base, an acid and a salt, a base and a salt,* and *a salt and a salt* are in contact, reversible reactions are taking place as should be expected. Sometimes, in respect to a given pair of reactions, one reaction is favored over the other; sometimes the two reactions are at equilibrium, depending upon the conditions at the moment: if a salt product is eliminated, reaction in the direction of its making is favored; if reabsorbed, the reverse reaction is favored. Some such specific reactions, and the physiological consequences, are presented in Chapter XXXI.

Questions

1. Summarize in the form of concise statements the chemical behavior, in general, that can be expected from (a) acids, (b) bases, and (c) salts in such contacts as are discussed in this chapter.

2. What, if any, reaction would you expect from each of the following contacts? If a reaction is to be expected, assemble the equation for the same; if no reaction is expected, tell why.

   a. Sour milk in an aluminium container.
   b. Iron rust in contact with vinegar.
   c. Silver knives, forks, or spoons in contact with sodium chloride solution.
   d. Ammonium hydroxide used in cleaning metal surfaces.
   e. Tarnished copper in contact with a metal polish containing oxalic acid.

3. Prepare a list of twelve or more possible contacts involving acids, bases, and salts (exclusive of the above-mentioned contacts) and tell whether or not a reaction is to be expected in each instance. Assemble equations for expected reactions and if no reaction is to be expected tell why. How many of these suggested contacts are of any practical significance so far as you know?

4. Why is it inadvisable to bring nickel-plated instruments into contact with bichloride of mercury solutions? What, if any, difference would you expect if the instrument were chromium plated? If the solution were silver nitrate? If the solution were magnesium sulfate?

5. Many commonly used cleaning powders contain sodium carbonate or potassium phosphate. What, if any, effect would you expect from the constant use of such solutions in cleaning aluminium dishes? In cleaning iron utensils?

6. To the presence of what substance or substances is the "hardness" of water usually due? Explain how washing soda functions in the "softening" of such water. What reactions take place when a soap (such as sodium palmitate) is used in hard water?

7. Lime water is the usual antidote suggested for poisoning by oxalic acid. How does it function? Sodium chloride is the antidote for silver nitrate. How does it function?

8. The following are among the substances normally present in the blood and lymph: carbonic acid, lactic acid, hydrochloric acid, sodium chloride, sodium bicarbonate, potassium sulfate. Assemble formula equations for various reactions that you would expect to be in operation within these media on the part of the above-mentioned substances.

9. Indicate which of the following reactions you would expect to be reversible and which not reversible, with reasoning:

   a. Ammonium hydroxide with hydrogen chloride.
   b. Sulfuric acid with sodium carbonate.
   c. Silver nitrate with sodium chloride.
   d. Cupric oxide with hydrogen chloride.

CHAPTER XVI

Solutions. Colloidal Solutions. Emulsions

Contrasting conditions. ***True solutions.*** It is a matter of common experience that many substances are soluble in water or some other liquids, meaning by "soluble" that when placed in contact with selected liquids either all or just portions of the substances quite automatically will in time become evenly distributed throughout said liquid to make the solutions. Such distributions are effected between sodium chloride and water, cane sugar and water, iodine and alcohol, and sulfur and carbon bisulfide.

As a result, every *solution is homogeneous*, that is, the solute or dispersed substance is in even distribution throughout the solvent or the dissolving medium. Furthermore, once the solution is obtained, no matter how long it may stand — whether it be for hours, days, or years — providing the same temperature is maintained and no solvent is allowed to evaporate, *no tendency toward separation of the solute from solvent* becomes apparent even though there may be considerable difference in their densities. Thus, a cane sugar and water solution, likewise an iodine and alcohol solution, will maintain their solution condition indefinitely with no tendency toward a settling out on the part of the denser cane sugar from the water or the denser iodine from the alcohol.

Another fact concerning solutions with a liquid as solvent and a solid as solute is that *both liquid and dissolved solute are able to pass through a filter very readily.* From this fact it must be concluded that the dispersed particles of solid solute are exceedingly small and, indeed, their size has been computed to be less than 1 millimicron (1 mμ) in diameter.[1] From a theoretical angle this means that they may even be as small as single molecules of the solute substances concerned.

Suspensions. In direct contrast with solutions is another variety of dispersion, exemplified by such systems as sand and water, raw starch and cold water, and fine flour and water, which can be obtained only through the mechanical aid of shaking or stirring and which exhibit a marked tendency toward separation — dis-

[1] 1 micron (μ) $= \frac{1}{1000}$ millimeter

1 millimicron (mμ) $= \frac{1}{1,000,000}$ millimeter

persed substance from dispersing liquid — immediately or very soon after the shaking or stirring is ended. Such a system is called a suspension. Moreover, when a suspension is subjected to filtration only the dispersing liquid can pass through the filter, any dispersed solid particles being held back. These nonfilterable particles which are characteristic of suspensions are greater than .1 micron (.1 μ) in diameter or more than one hundred times the diameter of the dispersed particles of a solution, and they can be distinguished either by the naked eye or certainly with the aid of a microscope.

Colloidal solutions. Then there are dispersions of a third type which range between solutions and suspensions and which are called *colloidal solutions.* Examples of such dispersions are albumen with water, soap with water, and "cooked" starch with water. In these systems the dispersed substances may show little or no evidence of separation from the dispersing liquid for a considerable period of time; and they pass through a filter more or less readily, depending upon whether the colloidal solutions approach true solutions in character or whether they approach the suspension end of the dispersion range. It should not be surprising, therefore, to learn that the particles which contribute to colloidal solutions range in size from somewhat greater than those which contribute to true solutions (diam. 1 mμ) to somewhat less than those which contribute to suspensions (diam. .1 μ). The theoretical deduction from these findings is to the effect that colloidal particles are either bunches of molecules or else very large single molecules, but that in either case they are considerably smaller than the dispersed particles of suspensions. They can be distinguished as separate particles with the aid of the ultramicroscope.

Thus there is no sharp line of differentiation between these three dispersion systems. But as to true solutions and colloidal solutions, if "borderline solutions" are disregarded, there are certain significant differences of importance between their behaviors that are worthy of attention. These two types of dispersions will, therefore, be presented in greater detail in the rest of this chapter.

TRUE SOLUTIONS

Defined. *A solution with a liquid as the dispersing medium* can be defined as *a system in which a substance is in even distribution throughout a liquid with no tendency whatsoever toward separation.* As has already been stated the dispersing liquid is commonly called the *solvent* and the dispersed substance the *solute.* Most frequently

the solute is a solid substance although it can be a liquid substance, as is true of a solution of alcohol in water, or a gaseous substance, as in the case of a solution of hydrogen chloride in water.

Distributed particles in

True solutions	*Colloidal solutions*	*Suspensions*
Less than 1 mμ in diameter.	1 mμ to .1 μ in diameter.	Greater than .1 μ in diameter.
Indistinguishable even with ultramicroscope.	Not visible under an ordinary microscope but detectable by ultramicroscope.	Can be distinguished by the naked eye or with the aid of an ordinary microscope.
Pass through filter paper, subject to diffusion through membranes (p. 214).	Pass through filter paper but do not diffuse through membranes (p. 219).	Do not pass through filter paper and are not subject to diffusion.
Dispersion is permanent.	Tendency toward separation of dispersed substance more or less delayed.	Separation of dispersed material is almost immediate.

The solutions with which we are concerned in this study involve liquid solvents, hence the above emphasis. Actually, however, the solution phenomenon has a broader scope in that solutions of gases in gases and solids in solids are possible. Air, for example, may be regarded as a solution of gases as may also illuminating gas mixture; and steel is essentially a solution of carbon in iron.

Theoretical explanation. Just why the solvent and solute portions of a solution effect and maintain an even distribution regardless of the difference in their densities is not known; but, as usual, failing the known explanation, theoretical concepts have been devised toward this end.

And so it is believed that within a true solution the dispersed particles of both solute and solvent are single molecules of the substances concerned. Furthermore, it is believed that these molecules are moving about with speeds which vary inversely with their relative weights, that is, the heavier the molecule the less is the speed with which it travels, while the lighter the molecule the greater is its speed. Consequently, despite the difference in relative weights of the molecules of solvent and solute they all move about among each other with the same kinetic energy. Naturally there are frequent collisions among the molecules and against sides of the container followed by rebounds, and in an attempt to reduce

these collisions to a minimum the heavier but slowly moving molecules and the lighter but more rapidly moving molecules eventually effect an even distribution in respect to each other (Fig. 65).

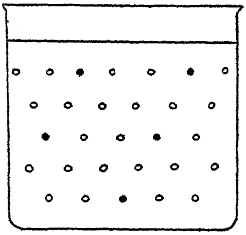


FIG. 65. In True Solution, Even Distribution of Solvent and Solute

And this distribution is maintained indefinitely because, although the heavier molecules do have a tendency to settle, their prompt collisions with other molecules moving with equal kinetic energy result in compensating reboundings on their part.

Properties of solutions. ***Boiling point of a solution.*** The presence of a nonvolatile * solute has the effect of raising the boiling point of the solution above that of the pure solvent. Water has a boiling point of 100° C. but when nonvolatile substances are dissolved in water the boiling point of the solution is above 100° C., the increase being proportional to the solution concentration. Thus, solutions in which one mole of sucrose (342.296 gm.), one mole of glucose (180.156 gm.), and one mole of glycerol (92.094 gm.) are respectively dissolved in 1000 grams of water (approximately 1000 cc.) have the same boiling point of 100.52° C., an increase of .52° over that of water alone. But it does not follow from this that water solutions of all nonvolatile substances in molal † concentrations have this same boiling point; in fact, if the solute is an acid, base, or salt the boiling point increase is even greater than .52°, the increase above this value varying with the specific acid, base, or salt. Accordingly, for a solution in which one mole of sodium chloride (58.454 gm.) is dissolved in 1000 grams of water the boiling point is 100.97° C.

* *The effect of volatile substances.* If the dissolved substance is more volatile than the liquid solvent, the boiling point of the solution is depressed below that of the pure solvent. Solutions of alcohol in water and of ether in water, for example, have boiling points below that of water alone: namely, below 100° C.

† *Molal solutions.* It should be observed that the above solutions on the basis of which boiling points are given, also freezing points presently, are slightly different from solutions on a molar basis (p. 226). Molar solutions contain one gram molecular weight of the solute in one liter of solution, whereas the above solutions are on the basis of one gram molecular weight of the solute in 1000 grams of water. Such solutions are called molal, *not* molar, solutions.

When a compound is very soluble its solution meets with considerable increase in boiling point over that of water. A saturated solution of sucrose at 90° C., for example, contains 4157 grams of sugar in 1000 grams of water and the boiling point of the solution

is 112° C. Certainly in cooking and in candy-making the high boiling point of this solution is of considerable importance, and a burn caused by a boiling sugar solution of such a high concentration is much more serious than one caused by boiling water alone.

Freezing point of a solution. The presence of a substance in solution in a liquid solvent has the effect of depressing the freezing point of the solution below that of the solvent alone. Water has a freezing point of 0° C., but water solutions of various substances have freezing points below this temperature, the extent of the depression being proportional to the concentration of the solution. Thus, solutions in which molar weights of ethyl alcohol, sucrose, glucose, and glycerol are respectively dissolved in 1000 grams of water have identical freezing points of − 1.86° C., a depression of 1.86° below that of water alone; solutions in which two moles of these compounds are dissolved in 1000 grams of water have like freezing points of − 3.92° C. Acids, bases, and salts in similar concentrations in water produce an even greater freezing point depression, the extent of which varies with the particular acid, base, or salt. For example: the solution in which one mole of sodium chloride is dissolved in 1000 grams of water has a freezing point of − 3.42° C.

If the compound is very soluble at these lower temperatures, the freezing point depression can become considerable. Such is the case with a saturated solution of sodium chloride in water the freezing point of which is − 21° C. This accounts for the fact that salt waters require considerably lower temperatures for freezing than do bodies of fresh water; it also explains why putting salt on an icy walk on a cold winter day or mixing salt with ice in the ice cream freezer causes the ice to melt.

Water solutions and diffusion through membranes. One or more components of a true solution are frequently subject to unequal diffusion through suitable membranes. This phenomenon is called osmosis and it is due to the osmotic pressure of the solutions concerned. Because of the importance of osmosis in respect to various solutions with *water* as the solvent, further discussion of this phenomenon will be confined to such solutions.

Membranes which are permeable to water but not to substances dissolved in water are called semipermeable membranes. Experimental results with such membranes are most significant. When such a membrane bag filled with a solution is tied securely about the base of a tube in such a manner that no leakage whatsoever can occur, and immersed in water, results are as follows: water is

able to pass through the membrane in both directions, but not the solute (Fig. 66). However, since the concentration of water in contact with the membrane is greater outside than inside the bag, more water passes into the solution than from the solution to the outside with the result that the solution volume inside the bag increases as will be evidenced by a rise of the solution in the tube. This inequality of diffusion of water through this membrane will continue, accompanied by a continual rise of the solution in the

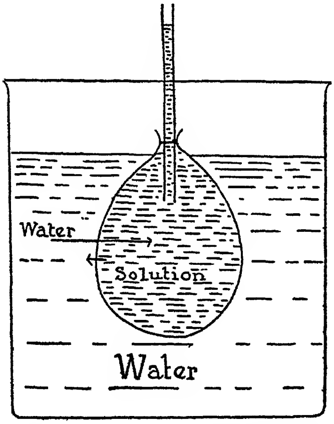


Fig. 66. A Semipermeable Membrane which Permits the Diffusion of Water Only

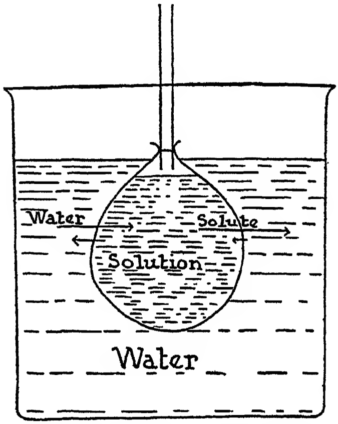


Fig. 67. A Permeable Membrane which Permits the Diffusion of Both Water and Solute

tube, until the pressure of the solution column in the tube — called the hydrostatic pressure — balances the excess pressure of the water entering the solution through the membrane over and above that of the water leaving the solution. This hydrostatic pressure varies with the concentration of the solution and becomes a measure of the osmotic pressure of said solution, since the greater the osmotic pressure of the solution the higher must be the column of water necessary to overcome the excess pressure of the pure water against that of the less concentrated water of the solution. Had conditions been reversed in the above demonstration — the water inside the bag and the solution outside — the inequality of water pressure against the membrane would be reversed, hence more water would pass from inside the bag through the enclosing membrane to the outside than contrariwise.

There are membranes, however, that are permeable to the dissolved solute as well as to the water. This can be demonstrated by filling such a parchment bag with a solution of sodium chloride, sucrose,

or other convenient and easily distinguishable solute and suspending the bag with solution in a vessel of water (Fig. 67). (Before the bag is put into the water it is advisable to assure one's self that there is no leakage of solution through some unobserved crack or fine break in the membrane.) In due time, it will be found that some of the solute, having passed through the membrane, can be detected in solution in the water surrounding the bag. The water, too, will pass through the membrane in both directions after the manner presented previously. Whether or not the increased volume in the bag will result in a rise of the solution in the tube will depend upon whether the bag was full with the solution to begin with.

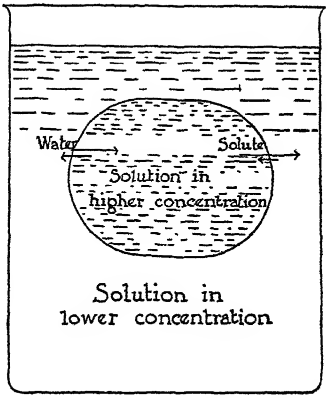


FIG. 68. A Permeable Membrane Separating Solutions of Differing Concentrations

Should solutions be present on both sides of such a membrane, but in differing concentrations, water and solute will diffuse through the membrane at different rates until either the diffusion meets with an equal counteracting resistance or the osmotic pressure of the two solutions is equal (Fig. 68). Should the more concentrated solution be inside the enclosing membrane with no outlet for an increase in solution volume, either the membrane must stretch continuously to accommodate the volume increase until the maximum is attained or else it must burst.

Importance of osmosis. This phenomenon of osmosis in respect to true solutions is of importance in many concerns, including the vital activities of both plants and animals.

In food preparation. The swelling of dried fruits, beans, etc., when soaked for some time in water, likewise the reverse shriveling of fresh fruits, such as peaches and prunes, when preserved in concentrated sugar solution, and of cucumbers when soaked in brine — all involve osmosis phenomena, the skins of the fruits and seeds serving as the permeable membranes.

In plants. It is in part due to osmosis through rootlet membranes that water and soluble salts are able to enter the plants from the soil and it is due to osmosis, too, that water and soluble compounds are able to enter plant cells from the sap and to leave the cells to join this circulating fluid.

In animals. Osmosis is also one functioning factor whereby water and soluble products of digestion are absorbed from the intestinal tract into the capillaries of the villi, and whereby water and various soluble substances are able to pass from the blood through successive membranes into the cells, and from the cells through various membranes either for distribution to other cells or on their way out of the body. It should be noted, however, that living membranes differ from dead membranes in that they appear to be able to select certain soluble substances for diffusion through them and to prohibit others. Thus, while the monosaccharids, glucose, fructose, and galactose, can pass through the intestinal membrane this membrane is impermeable to disaccharids which are also in true solution.

In therapeutic treatment. In general, solutions used for irrigation, and most importantly those for introduction into the blood stream, should be "isotonic" or solutions of equal osmotic pressure with the blood and the blood corpuscles. Why?

Theoretical explanation. Thus far the discussion as to the unequal diffusion of the components of a solution through membranes, or osmosis, has been from the factual viewpoint. Now for the reason as to why true solutions behave in this manner; and since the real reason is not known, once again it is necessary to resort to well-established theory. As previously, we shall present reasoning in respect to water solutions, although the same line would hold for other solutions with other liquid solvents.

It has been stated previously in this chapter that the distributed particles within a true solution are believed to be single molecules of the solute. Furthermore it is believed that the molecules of both water and solute are in rapid motion, which means that they are continually rebounding from each other or the sides of the container; consequently, when a membrane lies in their path, if it is permeable to the molecules, some of them will pass through it; if not permeable, the molecules will rebound.

The rest of the reasoned imaginings should be obvious. If water and the solution are separated by a strictly semipermeable membrane, the water molecules are able to pass through this membrane from both sides when they hit against it, but since the concentration of the water molecules against the membrane is greater on the side of the pure water than on the side of the solution — the solute molecules sharing contacts against the membrane with the water molecules on the solution side — more water molecules pass from the pure water to the solution than vice versa. The solute

molecules will, of course, impact against the membrane but are unable to penetrate it (Fig. 69).

Should the membrane be permeable to both water and solute, but separating solutions of different concentrations, while molecules of both water and solute will pass continuously through the membrane in both directions (Fig. 70) — more water molecules

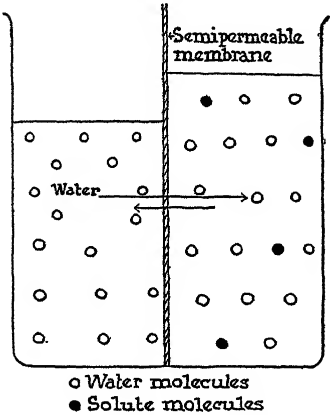


FIG. 69. A Membrane Permeable to Only Water Molecules

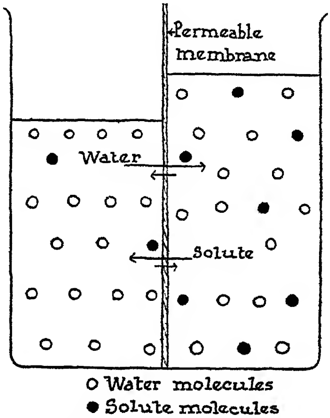


FIG. 70. A Membrane Permeable to Molecules of Both Water and Solute

will move from the solution of higher water concentration to that of lower water concentration, whereas more solute molecules will move through the membrane from the higher solute concentration to the lower solute concentration, and the increase in solution volume will be accordingly.

Only a very little has been possible in this chapter by way of pointing to some of the practical aspects of the boiling points and freezing points of solutions in comparison with those of water alone and of the unequal diffusion of just water or of water and other solution components through membranes. But to scientists these measured effects are of tremendous importance. For further information in regard to these phenomena the student must turn to more comprehensive texts in chemistry or to physical chemistries.

CONCERNING COLLOIDAL SOLUTIONS

The primary difference between colloidal and true solutions lies in the *size of the distributed particles* and the consequent degree of dispersion. This in turn results in certain typical differences in

the properties of true and colloidal solutions. However, as has already been pointed out, there is no sharp line of demarcation between these two types of dispersions. Indeed, in some instances the same substance is capable of appearing in either true or colloidal solution, depending upon conditions. On the other hand, there are substances which are able to form colloidal solutions but which are incapable under any conditions of providing particles small enough to form true solutions in any dispersion medium.

Properties of colloidal solutions in contrast to those of true solutions. *Light penetration.* True solutions with transparent liquids as solvents are likewise transparent since light passes directly through them save for some diffraction. As for colloidal solutions, some are visibly translucent, and they are translucent because light rays, upon effecting a partial penetration into the solution, are not permitted to get very far before they are reflected from surfaces of the numerous and sizable dispersed particles present. However, there are other colloidal solutions that may appear to the eye to be as clear and transparent as do true solutions since the distributed particles are not visible; but when a ray of light enters such a colloidal solution an opalescence appears which is due to the presence of particles too small to be seen but large enough to act as reflectors of light.

Tendency toward separation. In true solutions, it will be recalled, the solute remains in even distribution with no tendency whatsoever toward separation from said solution. And there are colloidal solutions in which substances appear to be in fairly permanent distribution with no separation becoming apparent until after weeks or months or longer. But there are other colloidal solutions in which the dispersions are far from permanent, the tendency toward separation of the distributed substance becoming apparent in a relatively short time. But in every instance as far as colloidal solutions are concerned, within a longer or a shorter period of time, separation of the dispersed particles from the dispersion medium will eventually come about.

Boiling point and freezing point. Again, in contrast with two other properties of true solutions: namely, their boiling point and freezing point (which for any given solution are always different from those of the solvent alone), the boiling and freezing points of a colloidal solution vary either only to an exceedingly small degree or none at all from those of the dispersion medium alone, depending upon whether the colloidal solution in the given liquid medium does or does not approximate a condition of true solution.

Thus, whereas the true solution formed from sugar and water has a boiling point and a freezing point different from that of water, the colloidal solution formed from albumen or starch with water has the same boiling and freezing temperatures as does water alone.

In respect to filtration and diffusion through a membrane. Substances in colloidal solution like substances in true solution can pass through an ordinary filter, more or less readily; but unlike substances in true solutions they are either absolutely incapable of diffusing through a membrane (such as cellophane or animal gut) or, as in the case of the smallest colloidal particles, diffuse to only a very slight extent.

In the laboratory this difference in diffusion possibility is taken advantage of for the separation of colloidal material from substances in true solution. In such practice, regarding water as the dispersion medium, the solution in which some substances are in true solution in water and some in colloidal solution is enclosed in a permeable membrane and the bag with solution is immersed in water. The rest of the story can be anticipated, since the substances in true solution are able to pass through the membrane into the water outside the same but not the substances in colloidal solution.

This process of separating a colloidal substance from a substance in true solution, through the agency of this diffusion through a membrane, is sometimes called dialysis.

Biologically this difference in diffusion possibility as to substances in true and colloidal solutions is of vital importance on the part of plants and animals. The water of the sap of plants and of the blood of animals holds some substances in true solution and others in colloidal solution but only the substances in true solution are able to enter the cells. On the other hand, within the cells of both plants and animals there are substances held in colloidal solution that must be kept there if cell activities are to proceed normally, and, fortunately, being colloidal, these substances are incapable of escaping from said cells.

Explanation for some of these properties. As has already been said (p. 210), *colloidal particles are larger and heavier than those in true solutions* and it is believed that this is because these particles are either small or large aggregates of molecules as may be true of the colloidal particles of starch, or possibly in some instances they may be massive single molecules such as most protein molecules (Fig. 71). Moreover, it is known that *most dispersed colloidal particles are electrically charged,* with all particles of any given colloid carrying like charges.

Consequently, both the relatively heavy weight and the effect of the electric charge must be considered in seeking an explanation for the behavior of these colloidal particles in solution. Particles carrying like electric charges repel each other. As a result, colloidal particles carrying like charges, in their effort to keep away from one another, tend to effect a relatively even distribution throughout

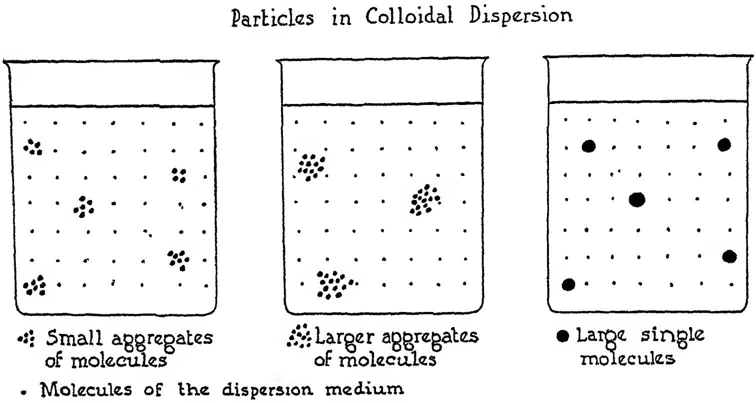


FIG. 71

the dispersion medium. At the same time, because of the greater weight of these colloidal particles in relation to the weight of molecules of the dispersion medium, usually those of water, they have a tendency to precipitate. Of course the kinetic energy of the more rapidly moving molecules of water, or other dispersion medium, is able to check this downward movement of the colloidal particles but not to prevent it entirely; therefore, although the heavy colloidal particles may in some instances be held in suspension for a considerable time, sooner or later separation will occur.

It is more especially the *size of the particles* that accounts, theoretically, for the behavior of colloids in respect to diffusion through membranes. Most colloidal particles are believed to be too large to squeeze between the molecules of membranes, only such as approximate in size the dispersed particles of true solutions being able, occasionally, to accomplish this act.

For example, one of the reasons why cooked starch and most proteins of the food mass are not able to pass through the intestinal membrane into the blood and why glycogen and cell proteins cannot diffuse through cell membranes into the lymph is believed to be due to the inability of their relatively very large single molecules or molecule aggregates to work their way between the molecules comprising the intestinal and cell membranes respectively.

But there is reason to believe that molecules of egg albumin,[2] lactalbumin, and some of the intermediate products of protein digestion approach the size of particles capable of true solution and are, therefore, able to diffuse through some membranes to a slight extent. Herein may lie an explanation for the sensitivity of an occasional person to these proteins in his food since it is believed that the intestinal membrane of such an individual is somewhat permeable to these protein molecules which normally cannot diffuse through the intestinal membrane.

MORE CONCERNING SOLUTIONS

Various liquid solvents. ***Water the best solvent.*** Water is the best known solvent in that it dissolves more substances to an appreciable extent than any other liquid. Indeed, strictly speaking, no substance is absolutely insoluble in water; "insoluble" being merely an easy way of saying "soluble only to an exceedingly slight degree."

This marked solvent property of water is occasionally a nuisance but it is in many ways advantageous. It is a nuisance, for example, when chemically pure water is desired, an aim which is difficult to achieve since naturally occurring water has greater or less quantities of many substances dissolved in it. But it is advantageous in the use of water as a cleansing agent for sugar and some fruit stains; it is advantageous, too, in the use of water as a carrier of substances in cookery, of drugs and disinfectants for their respective purposes, of chemicals in the laboratory and of substances in manufacturing concerns.

Solvents other than water. Many substances which are only slightly or even inappreciably soluble in water are readily soluble in other liquid solvents. Iodine, for example, is only slightly soluble in water but is quite soluble in ethyl alcohol. And, both ethyl alcohol and methyl alcohol are used in the industries as solvents for various substances that are insoluble in water. Ethyl alcohol is also used as a solvent for some drugs, flavors, and perfumes (p. 312). Fats are insoluble in water but soluble in ether; they are also soluble in liquid hydrocarbons, hence in benzine and gasoline which, it will be recalled, are hydrocarbon mixtures (p. 292).

Extent of solubility. ***Usually limited.*** There is no limit to the solubility of some substances in selected solvents. This is true of

[2] The student should distinguish between egg albumen and egg albumin. The former is the mixture of proteins of egg white, the latter is one of the several proteins of egg white that is related to other proteins likewise classed as albumins (p. 419).

ethyl alcohol with water and of glycerol with water which are soluble in each other in all proportions. But, as a rule, a given quantity of water, or of any other liquid solvent, is able to hold in solution varying weights of a given substance only up to a definite limit under given temperature conditions. For example, 100 cc. of water at 20° C. is able to hold in solution varying quantities of cane sugar up to the limit of 203.9 grams, from then on, providing the solution is kept at 20° C. and even though a considerable excess of the undissolved cane sugar may be present, the quantity in solution is maintained at this constant of 203.9 grams in 100 cc. of water.

Unsaturated and saturated solutions. In order to differentiate between solutions which can and cannot dissolve more of a solute substance the expressions unsaturated solution and saturated solution have come into use. Thus a *solution is unsaturated* when upon contact with some of the undissolved solute it is able to take more of the same into solution. But if on contact with undissolved solute the solution is unable to dissolve more of the same then the *solution is saturated.* Accordingly, all cane sugar and water solutions which contain less than 203.9 grams of this solute in 100 cc. of water at 20° C. are unsaturated, but when this limit is reached the solution is saturated at this temperature.

The quantity of a substance that is held in solution at saturation varies with the substance and with the solvent. This fact is exemplified in the following table, the stated solubilities of the substances specified being the quantities of the substances in water solution at saturation. In this connection the meaning of the expressions *slightly soluble* and *very soluble* should now be apparent since they refer to whether little or much of the substance is able to dissolve in the given solvent before the solution attains saturation. Thus, as reference to the following table reveals, iodine is only slightly soluble in water whereas silver nitrate is very soluble in this solvent medium.

Varies with temperature of solution. Another factor which determines the quantity of a substance that is able to dissolve in a given solvent before the solution reaches saturation is the temperature of the solution. As a rule the solubility of *solid substances* in liquid solvents increases with an increase in the temperature of the solution, a fact which is again exemplified by means of the data provided in the following table. But, as with most good rules, there are exceptions, and so a few solid substances, calcium hydroxide and calcium sulfate among them, are more soluble in water

at lower than at higher temperatures. If the solutes are *gaseous substances*, they are always less soluble as the temperature of the solution increases and vice versa. This fact is illustrated in the accompanying table with definite quantitative data as to nitrogen, oxygen, and carbon dioxide in water solution.

Solid substances	*Solubility in grams in 100 ml. of water*	
	At 20° C. (ordinary temperature)	*At 100° C.*
Barium sulfate	.00024	.00039
Boric acid	4.8	28.7
Calcium carbonate	.0014 (at 25° C.)	.0018 (at 75° C.)
Calcium chloride	59.5 (at 0° C.)	159.0
Calcium hydroxide	.165	.077
Calcium oxalate	.00068 (at 25° C.)	.0014 (at 95° C.)
Calcium phosphate	.002	——
Calcium sulfate	.1759 (at 0° C.)	.1619
Iodine	.029	.078 (at 50° C.)
Mercuric chloride	6.1	61.3
Mercurous chloride	.5	25.0
Potassium hydroxide	112.0	178.0
Potassium iodide	144.0	208.0
Silicon dioxide	Insoluble	Insoluble
Silver chloride	.000015	.0021
Silver nitrate	222.0	952.0
Sodium tetraborate (borax)	2.83 (0° C.)	201.4
Sodium bicarbonate	9.6	16.4 (at 60° C.)
Sodium chloride	36.0	39.8
Sodium hydroxide	109.0	347.0
Sucrose (cane sugar)	203.9	487.0
Gaseous substance	*In 100 ml. of water at given temperature under standard pressure*	
Carbon dioxide	179.7 cc. at 0° C.	90.1 cc. at 20° C.
Chlorine	310.0 cc. at 10° C.	177.0 cc. at 30° C.
Hydrogen	1.93 cc. at 0° C.	.85 cc. at 80° C.
Hydrogen chloride	82.3 gm. at 0° C.	56.1 gm. at 60° C.
Oxygen	4.89 cc. at 0° C.	2.61 cc. at 30° C.
Nitrogen	2.35 cc. at 0° C.	1.55 cc. at 20° C.

Aids in the preparation of solutions. ***Increasing area of contact.*** Obviously in the preparation of any solution the greater the area of contact between solvent and solute the more rapidly is the solution accomplished. For this reason finely divided solids dissolve more rapidly than do the same substances in coarser particles. Stirring or shaking also hastens solution-making by effecting a more thorough distribution of the solute in contact with the solvent.

Temperature aid. When a substance is considerably more soluble at higher than at lower temperatures its solution can be brought about more speedily

in the hot solvent than in the solvent at room temperature. Advantage can be taken of this favoring condition in making water solutions of mercuric chloride (see table) and boric acid. But for making solutions of substances which are more soluble in cold than in the hot solvent, such as calcium hydroxide in water, obviously the lower temperature is the more advantageous.

When some substances, such as sodium hydroxide, enter solution in water considerable heat product, called the heat of solution of the substance, is made. When such is the case, it is unwise to use hot water in making the solution.

However, no general rule can be formulated as to the temperature most desirable for making solutions as speedily as possible, but tables of solubilities of substances at different temperatures are helpful in this connection and can be consulted with advantage.

Supersaturated solution. In some instances when a solution has been saturated at a high temperature with a solid solute the entire solute will remain in solution as the temperature of the solution is lowered — providing no undissolved solute is in contact with the solution. Such solutions at such lower temperatures are *supersaturated.* Thus, if 219.5 grams of cane sugar (sucrose) are dissolved in 100 cc. of water at 30° C. and the solution cooled to 20° C. without any accompanying precipitation of this solute, the solution will be supersaturated at this lower temperature (p. 223). Supersaturated solutions are frequently very difficult to maintain since a slight disturbance, such as shaking or stirring, or the introduction of a solid particle, especially if it be a particle of the solid solute itself, will give rise to a precipitation from the solution of the solid solute in excess of saturation at the lower temperature.

Oxalic acid may be cited as an example of a substance that is capable of yielding a supersaturated solution in water. At 15° C. a saturated solution of oxalic acid contains 9.5 grams of the solute per liter of solution. At higher temperatures considerably more concentrated solutions of oxalic acid can be obtained (at 90° C. 120 grams per liter of solution). Therefore, if a quantity somewhat in excess of 9.5 grams of oxalic acid is dissolved in a liter of hot water and the solution is then cooled slowly, without in any way jarring or disturbing it, the entire quantity of this solute may be retained in solution even when cooled down to the temperature of 15° C. When such is the case, the oxalic acid solution at 15° C. is supersaturated. However, when shaken or, better, when a crystal of solid oxalic acid is added, the excess acid above saturation at 15° C. will in time precipitate.

Dilute and concentrated solutions. Solutions are dilute or concentrated depending upon whether relatively little or much of the

solute is present in a given volume of the solution. Some substances are very soluble in water and are therefore capable of yielding very concentrated solutions in this solvent. This is true of sodium hydroxide and silver nitrate. Other substances, such as mercuric chloride and calcium hydroxide, are so slightly soluble that it is impossible to obtain them in any save very dilute solutions in water.

Sometimes dilute and concentrated solutions are called weak and strong solutions respectively. Such expressions in this connection are ill-advised and confusing since "weak" and "strong" are reserved for different and very specific usages which will be considered later.

Methods of expressing exact concentrations. Various standards are used for solutions of more or less exact quantitative concentrations. Among those in common use are the following:

Solution concentration on a percentage basis. Solutions are frequently made up on a percentage basis and their concentrations expressed as 10 per cent, 50 per cent, 1 per cent solutions, etc. If such solutions are accurately prepared, both the solute and solvent must be measured on a common *weight* basis, thus on a gram basis a 1 per cent solution of sodium chloride is one which contains one gram of sodium chloride in every 100 grams of the solution. For convenience, however, the solvent, especially when water is used, is sometimes measured by volume rather than by weight. Such solutions are approximate, the degree toward accuracy depending upon the density of the solvent.

Again, with water as the solvent, although 1 cc. of water is actually 1 gram of water only when at 4° C., at usual temperatures this volume of water is so close to 1 gram (at 20° C. .998 gm., at 100° C. .959 gm.) that for many solution purposes the water is measured by volume in cubic centimeters instead of by weight in grams, but the solute measured in grams; and the solution thus made will be close to the specified percentage concentration. But should the solvent used have a density which varies markedly from that of 1 gram per cubic centimeter the solution made up after this manner will be quite inaccurate as to percentage concentration unless the density of the solvent be taken into consideration and the calculations as to the requisite volume be made accordingly.

Ratio basis. Solutions are sometimes made up on a ratio basis of weight of solute to solvent as 1 to 5, 1 to 25, 1 to 1000, etc. Should volume be used for measuring the solvent, the same obser-

vations apply to the accuracy of solutions made up on this basis as to those prepared on a percentage basis.

Solutions on a percentage, also on a ratio, basis have no chemical significance but they are quite appropriate for many desired purposes including therapeutic, industrial, and laboratory uses.

Solution concentrations which do have a chemical significance are called molar and normal solutions.

Molar solutions. *One mole* of a substance is one gram molecular weight of the substance. With this information at hand we are in a position to define *a solution of molar concentration as one which contains one mole of the solute in one liter of solution.* For example: a molar solution of sodium chloride contains 58.454 grams of this solute in one liter of solution; a molar solution of silver nitrate contains 169.888 grams of this compound in one liter of solution. More concentrated or more dilute solutions can be prepared on this basis as multiples or fractional parts of a molar solution. Thus, a two-molar solution contains two moles or two gram molecular weights of solute in each liter of solution whereas a tenth-molar solution contains one-tenth of the gram molecular weight of the solute in each liter of solution.

A form of shorthand has come into use for representing these concentrations. Accordingly, a solution of molar concentration is represented by 1 M, a two-molar solution by 2 M, a solution containing five moles of solute per liter of solution by 5 M. Similarly with more dilute solutions, the concentration of a solution which contains one-half mole of solute per liter is represented either by .5 M or by M/2, a tenth-molar solution is represented by .1 M or M/10, a fifth-molar solution by .2 M or M/5, etc. Examples of some of these solution concentrations on a molar basis are as follows:

M (molar) solution

Sodium chloride....................	58.454 grams	in 1 liter of solution.
Silver nitrate......................	169.888 grams	

2 M (two molar) solution

Sodium chloride....................	116.908 grams	in 1 liter of solution
Silver nitrate......................	339.776 grams	

.1 M (tenth molar) solution

Sodium chloride....................	5.8454 grams	in 1 liter of solution.
Silver nitrate......................	16.9888 grams	

Solution concentrations on this basis have a chemical significance since molecular weights serve as measuring units for substances as

they become involved in chemical reactions. Consequently, if the number of molecular weights of substances mutually involved in a given chemical reaction are known, it becomes possible to measure out such solution volumes, made up on a molar basis, as will contain the exact reacting weights of said substances. Thus:

Sulfuric acid	+	Sodium hydroxide	$\longrightarrow$	Water	+	Sodium sulfate
H_2SO_4	+	$2\,NaOH$	$\longrightarrow$	$2\,H_2O$	+	Na_2SO_4
1 Molecular weight		2 Molecular weights				

Therefore, solution volumes which contain such weights of sulfuric acid and sodium hydroxide as will exactly react with each other to make water and sodium sulfate are as follows:

Sulfuric acid		*Sodium hydroxide*
1 liter of M solution	to	2 liters of M solution
or, 10 cc. of M solution	to	20 cc. of M solution
or, 10 cc. of .1 M solution	to	20 cc. of .1 M solution

Molecule concentrations in such solutions. Since one mole of every substance is believed to include 6.06×10^{23} molecules of the substance, it follows that one liter of a molar solution must contain 6.06×10^{23} molecules of the substance concerned (p. 109), while one liter of a half-molar solution must contain one-half this number of molecules of said substance, etc. Which being true, it will obviously follow that equal volumes of solutions of various substances of the same molarity must contain equal numbers of molecules of these substances.

Normal solutions. Solutions on a normal basis apply only to acids, bases, and salts and they are really concerned with concentrations of the radicals provided within these compounds rather than concentrations of the compounds in themselves. Accordingly, *a normal solution is such a solution concentration of an acid, base, or salt, as provides within one liter one-valent quantities in grams of the two radicals concerned.* Thus one liter of normal solutions of hydrochloric acid, calcium hydroxide, and sodium phosphate have concentrations as indicated on the following page.

Solutions of greater or less concentration but still on a normal basis are also frequently used. Shorthand representations for solution concentrations on a normal basis are as follows: N, 2 N, 5 N, obviously in respect to normal, two-normal, and five-normal concentrations; 1/2 N or .5 N and 1/10 N or .1 N in respect to solutions of half-normal and tenth-normal concentrations.

While presenting solutions known to the chemist as normal solutions it is well to note that the so-called *normal* or *physiological* solution of sodium chloride commonly used in hospital practice does not belong in this class. There is no chemical significance in the term "normal" used in this connection. The concentration of such solutions is 8.5 grams of sodium chloride per liter of solution, this being approximately the concentration of the salts normally present in the blood stream. Therefore, the term *physiological salt solution* is to be preferred for such a salt solution since it is more descriptive of the concentration that is meant and avoids the danger of confusion with the normal solution of chemical significance.

Formula for molecular weight of compound and valences of radicals therein	*Portion of molecular weight of compound to contain one-valent quantities of radicals*	*One liter of normal solution contains*
$\underbrace{\underset{1.008}{H'}\quad\underset{35.457}{Cl'}}_{\text{Molecular weight}}$	1 Molecular weight	*1 Gm. M.W. of hydrogen chloride* H′ 1.008 gm. hydrogen radical Cl′ 35.457 gm. chloride radical
$\underbrace{\underset{40.08}{Ca''}\quad\underset{2 \times 17.008}{(OH)_2'}}_{\text{Molecular weight}}$	$\frac{\text{Molecular weight}}{2}$	*1/2 Gm. M.W. of calcium hydroxide* Ca″/2 20.04 gm. calcium radical OH′ 17.008 gm. hydroxide radical
$\underbrace{\underset{3 \times 22.997}{Na_3'}\quad\underset{94.98}{(PO_4)'''}}_{\text{Molecular weight}}$	$\frac{\text{Molecular weight}}{3}$	*1/3 Gm. M.W. of sodium phosphate* Na′ 22.997 gm. sodium radical $PO_4'''/3$ 31.66 gm. phosphate

Normal solutions of acids and bases. Normal solution of an acid is many times defined from the standpoint of the concentration of the hydrogen radical which is common to solutions of all acids; while normal solution of a base is defined from the standpoint of the concentration of the hydroxide radical which is common to solutions of all bases. From these standpoints, then, *a normal solution of an acid is a solution which contains a one-valent quantity, or 1.008 grams of hydrogen radical in one liter of solution;* whereas *a normal solution of a base is a solution which contains a one-valent quantity, or 17.008 grams, of hydroxide radical in one liter of solution.*

And, of course, modifications of normal solutions of acids and bases, such as half-normal and tenth-normal solutions, are of commensurate concentrations. Solutions of normal and tenth-normal concentrations of specified acids and bases are as follows:

	In 1 liter of normal solution	*In 1 liter of tenth-normal solution*
$H'NO_3'$	63.016 gm. nitric acid	1/10 of 63.016 gm. nitric acid
63.016	H', 1.008 gm. hydrogen radical	H'/10, .1008 gm. hydrogen radical
$H_2'SO_4''$	1/2 of 98.076 gm. sulfuric acid	1/20 of 98.076 gm. sulfuric acid
98.076	H', 1.008 gm. hydrogen radical	H'/10, .1008 gm. hydrogen radical
$H_3'PO_4'''$	1/3 of 98.004 gm. phosphoric acid	1/30 of 98.004 gm. phosphoric acid
98.004	H', 1.008 gm. hydrogen radical	H'/10, .1008 gm. hydrogen radical
$Na'OH'$	40.005 gm. sodium hydroxide	1/10 of 40.005 gm. sodium hydroxide
40.005	OH', 17.008 gm. hydroxide radical	OH'/10, 1.7008 gm. hydroxide radical
$NH_4'OH'$	35.048 gm. ammonium hydroxide	1/10 of 35.048 gm. ammonium hydroxide
35.048	OH', 17.008 gm. hydroxide radical	OH'/10, 1.7008 gm. hydroxide radical
$Ca''(OH)_2'$	1/2 of 74.096 gm. calcium hydroxide [3]	1/20 of 74.096 gm. calcium hydroxide [3]
74.096	OH', 17.008 gm. hydroxide radical	OH'/10, 1.7008 gm. hydroxide radical

COLLOIDS AND GEL FORMATIONS

Colloids are capable of forming gels. The property of forming gels is a characteristic peculiar to colloidal systems. Indeed the name *colloid* (from a Greek word meaning "glue") was first applied to such systems in recognition of this property by Thomas Graham (1805–1869), a scientist who contributed greatly to the knowledge of this branch of chemistry study.

A gel, as distinguished from such colloidal solutions as have been discussed previously, is a colloidal system which, although containing a considerable portion of liquid, possesses a greater or less degree of rigidity. Gels may vary all the way from fluid jellies which flow on slight pressure to gels of decidedly rigid structure. This rigidity is believed to be due to a very definite structure developed within the dispersed system, that is presumably brought about by the adherence of some of the colloidal particles to one another whereby they form fibrils, and these fibrils serve to enmesh a more dilute colloidal solution. Familiar examples of gels are fruit jellies, cooked starch, and heat-coagulated egg white.

Gel formation. Two methods are in common use for making gels and both are familiar. One of these methods consists of allowing suitable substances, such as starch, gelatine, or soap, to soak

[3] These would be the concentrations of normal and tenth-normal solutions of calcium hydroxide if it were sufficiently soluble (p. 229).

in contact with water (or another desired dispersion medium) until the colloidal material has gradually absorbed the fluid and swelling has occurred with the production of a jelly-like mass.

The second method consists of first preparing a colloidal solution of the material desired for the gell, then altering the temperature, and in some instances the concentration of acids, bases, or salts present, and finally allowing the solution to stand undisturbed until the gel gradually "sets." The gel which follows upon the cooling of cooked starch is a familiar example of this process; likewise the gel of gelatine mould.

Some recipe procedures call for a combination of the two methods, cold water being used first until the maximum "swelling" of the material has taken place, then hot water to secure a colloidal solution followed by a cooling until the gel "sets."

The aging of gels. In the course of time gels show certain characteristic changes, notably the separation of some of the liquid from the gel mass with a consequent concentration of the solid material. The fluid which thus exudes from the gel is not water alone, but is a dilute solution of components that contribute to the gel mass. This process is known as *syneresis* and may be regarded as the reverse of the absorption which previously took place in the gel formation.

Some items concerning the practical importance of gels. Both gel formation and the syneresis attendant upon the aging of gels are of frequent occurrence and are often of practical importance.

Various *cookery procedures* involve the making of gels, typical examples being the preparation of cornstarch or gelatine moulds, the making of fruit jellies, of custards, and of junkets. And none of these gels can be kept for any length of time without showing characteristic evidence of age; drops of moisture will eventually collect on the surface of jellies, custards will "break," and curds will separate from the whey of junket. Bread-making involves obtaining a protein-starch gel of a definite structure, and when bread becomes "stale" changes such as have been described in the foregoing as syneresis take place. Thus, if bread is kept in a tight tin box so that evaporation of water is checked, moisture collects on the surface of the loaf. This moisture has come from the bread itself and if allowed to evaporate the bread will become dry throughout. However, it is interesting to note that some colloidal systems, including bread, are capable of holding more moisture at higher than at ordinary temperatures; hence, if the moist bread is heated for a short time in the oven, some of this

moisture will be reabsorbed, thereby partially restoring the bread to its original condition and producing a "freshening" effect.

The preparation of gelatine and agar slants and culture plates in the *bacteriological laboratory* involves gel formation; and all laboratory workers are familiar with the syneresis, characterized by the appearance of drops of moisture and the shrinkage of the material within the tubes and plates, that occur as culture media age.

Various mucilages, glues, and pastes, whether prepared in the household or industrially, may be cited as other examples of gels.

Physiological importance. Gels also contribute to cell structure. About seventy per cent of the content of the body is water and the greater part of this water is held within the cells of muscle, nerve, and other tissues; but despite this large supply of water the content of the cells is in a semifluid condition due to the presence of colloidal materials in gel formation. It is claimed by some that certain of the changes which accompany old age, as for instance the changes in blood vessel walls known as arteriosclerosis, are essentially the result of the aging of a colloid system.[4] The clotting of blood involves the formation of a gel; and the subsequent exudation of serum, which is characteristic of the hardening and drying of the clot, is another example of syneresis.

EMULSIONS AND EMULSIFYING AGENTS

What is an emulsion? Liquid substances which are not capable of forming true solutions in a given solvent can sometimes become dispersed throughout said solvent in the form of an emulsion. The dispersed liquid particles in an emulsion may be of colloidal dimensions but frequently they are of suspension dimensions and large enough to be discernible to the naked eye or under an ordinary microscope. An emulsion can, therefore, be defined as a mixture of two mutually insoluble liquids one of which is dispersed in the other in more or less finely divided particles. The most commonly occurring emulsions are those of water with oily substances such as fats, liquid hydrocarbons, or mixtures of liquid hydrocarbons (p. 292).

Emulsifying agents. Although an emulsion can be easily obtained by mixing and shaking the two liquids together, it is difficult to maintain unless some means is provided to check the marked tendency on the part of the two liquids to separate. Such a means is provided through the agency of selected substances which, when

[4] R. A. Gortner, *Outlines of Biochemistry*, John Wiley & Sons, 1938, p. 274.

added to the emulsion, are capable of prolonging the period of suspension. These substances are known as emulsifying agents or stabilizers. To make this more meaningful let us consider what happens when oil and water are mixed with and without the presence of a stabilizer. Upon thorough shaking of the mixture a suspension of small oil droplets is produced, but if this mixture is allowed to stand, within a very short time practically all of the oil will be found in a layer on top of the water. However, if a little soap is added and the mixture is again thoroughly shaken, a much more lasting emulsion can be obtained with the soap functioning as an emulsifying agent.

In general, emulsions are characterized by a "milky" appearance after the manner of milk and cream and the milky secretions of certain plants, such as the milkweed or the poppy; and all of these secretions are examples of naturally occurring emulsions.

Functioning of emulsifying agents. The functioning of the emulsifying agent as an aid in prolonging the life of the emulsion is believed to be due to its ability to collect in a thin film at the surface of the suspended particles, thereby preventing them from coalescing to make larger drops. In order that it may function in this way the emulsifying agent must be a substance which has a marked adsorptive attraction in respect to one or the other of the liquid components of the emulsion. In many instances, though by no means all, the emulsifying agent is a substance which is capable of colloidal dispersion with one of the liquids involved in the emulsion. For example: sodium and potassium soaps; resins and certain gums, such as gum acacia and Irish moss; proteins, such as albumin, gelatin, and hemoglobin; dextrins and starches; cholesterol (p. 371) and lecithins (p. 373) — all form colloidal solutions with water and all are stabilizers for water and oil emulsions. And the effectiveness of these emulsifying agents is attributed to the semisolid films which they form at the interfaces between the two liquid components of the emulsion.

But sometimes certain finely divided and insoluble solids — that is, solids not capable of forming colloidal solutions with either liquid contributing to an emulsion — function as emulsifying agents; and the more finely divided such a solid substance is, the greater is its stabilizing effect as to the emulsion concerned. Fuller's earth and kaolin are examples of such insoluble solid emulsifying agents for water and oil emulsions; and they are used for just this purpose in making water and mineral oil emulsions for insecticidal sprays. And again, such an insoluble emulsifying agent

— as is true of any emulsifying agent — must be attracted to one of the two liquids contributing to the emulsion in such a manner that a thin film of the finely divided solid is formed around the suspended droplets of this liquid component of the emulsion, thereby checking their tendency to coalesce. In the above-mentioned water-in-oil emulsion either the Fuller's earth or kaolin is attracted to and forms such a protective layer about the oil droplets.

Surface tension a factor in making emulsions. Various theories have been advanced in attempts to account for the behavior of emulsions and for the functioning of emulsifying agents. And factors which are believed to play an important part in the behavior of emulsions and in the functioning of emulsifying agents are the *surface tensions* of the liquids involved and changes which can be effected in relation to these surface tensions.

A liquid, although subject to changes in shape depending upon the shape of the container, has definite *surface boundary*, and at this surface it behaves as if it were covered by a more or less elastic film or "skin" maintained under tension. The cohesive force which exists between particles throughout the entire bulk of the liquid is more marked at its surface, and it is this surface effect that is known as "*surface tension.*" One of the manifestations of this force is the tendency on the part of a liquid to assume the form which will present the least surface area; thus small particles of a liquid tend to form spheres, whereas droplets coming in contact with one another tend to be drawn together and to unite to form single larger particles, thereby decreasing the total surface area.

In general, liquids which are mutually insoluble, as is the situation in respect to the liquids in an emulsion, exhibit a high degree of interfacial or surface tension where they come in contact with each other. The cohesive force between particles of each of the liquids contributing to an emulsion tends to make these particles coalesce and in this way a gradual separation of the two liquids is effected.

Therefore, for stabilizing an emulsion, it is first necessary to overcome to some extent the forces of surface tension in order to obtain a fine dispersion; it is further necessary to prevent, as far as possible, the operation of these forces if the dispersion is to be maintained. The addition of a substance which lowers the surface tension of either one of the liquids to a marked degree will function to stabilize the emulsion. For example, sodium and potassium soaps markedly lower the surface tension of water and it is for this reason that these substances are effective emulsifying agents for oil-in-water emulsions. Moreover, substances which thus lower the surface tension of a liquid tend to collect at its surface — at the surface of the liquid and its container, at the liquid-air surface, and at the interfacial surface between the two liquids. It is this collection of the emulsifying agent at the interfacial surface of the two liquids which is believed to account for its distribution in a thin film around the droplets of the dispersed liquid, thus interfering with their coalescence.

Energy expenditure, a factor in obtaining emulsions. Another condition essential to obtaining a lasting emulsion is that the suspended liquid be broken up into very small droplets, the smaller the better. This necessitates the expenditure of energy to overcome the cohesive force existing between particles of the same substance which tends to hold them together in a continuous mass. This end can be accomplished in a variety of ways, such as shaking, stirring, whipping, rubbing, etc. And, again, if water and oil are the two liquids involved, the greater the proportion of oil to water the greater the energy that must be expended to secure a lasting emulsion. It has also been found that intermittent shaking or stirring is more effective for the making of an emulsion than is continuous agitation.

For this energy aid in emulsion-making an electrically driven machine is obviously able to produce the desired emulsion more effectively than can be accomplished by hand. The process of homogenization that is used extensively in large-scale operations for the preparation of lasting emulsions secures an exceedingly fine dispersion by means of forcing a mixture of the two liquids through very fine tubes under high pressure.

Practical uses of emulsions. Emulsions are of importance in a great variety of daily concerns of which only a few can be suggested here. *In ordinary cleaning* operations the most common agent for the removal of fats and oils is soap and water, the soap being provided to function as an emulsifying agent, since neither fats nor oils are soluble in water. It follows, then, that an important part of the cleaning procedure consists in obtaining a good emulsion, and to this end the soap must be used in sufficient concentration to produce an effective film around the fat droplets. (It is quite as possible to use too much soap as it is to use too little; furthermore, the soap that is used in excess of the need is not only wasted but can actually decrease the stability of the emulsion.) The hand-rubbing or the agitation produced in the washing machine is also important in effecting the desired dispersion of the grease throughout the soapy water. In this manner fats and oils can be removed from the skin, garments, and utensils by way of an emulsion which could not possibly be accomplished through the agency of water alone.

Emulsions have an important place *in cookery*. The making of mayonnaise dressing involves obtaining an emulsion on the part of oil and water mixture, the latter being provided either by the vinegar or lemon juice. And the process employed is a familiar

one. The two liquids are thoroughly mixed by beating, the oil being thus broken into finer and finer droplets; and egg yolk is added, the proteins of which function as an emulsifying agent for the oil and water emulsion. However, the proteins of egg yolk are not the only stabilizers that are possible for mayonnaise; in some commercial preparations of this dressing starch is introduced to serve this end. In the making of French dressing gelatine can be used to advantage as an emulsifying agent for the fat and water dispersion. In the preparation of gravies and various food sauces cooked starch, provided by the flour or cornstarch, functions to hold the fat and water in emulsion dispersion. An interesting example of a modern use of emulsification has to do with the means for obtaining sweet milk and cream for food uses on battleships on long cruises and for armed forces in any locations where frequent fresh supplies are out of the question. In anticipation of such a need, stocks of dried skim milk and butter fat are kept on hand, and when either milk or cream is desired it is obtained by assembling an emulsion from an appropriate mixture of water, fresh butter, and dried milk through the aid of an homogenizer.

In pharmacy, also, emulsions have their uses, notably to render certain oily medications, such as mineral oil and cod liver oil, somewhat more palatable. The emulsifying agents used for this purpose include agar and gum acacia.

Emulsions are of importance physiologically. And as will be presented later (p. 450), the emulsification of fats in the digestive tract is of great importance as a means for bringing fats, water, and digestive enzymes into contact with each other, in this way favoring the digestive process. The emulsion phenomenon is also important as the means provided by nature for maintaining the suspension of fats in the lymph and blood for transportation to the cells.

Questions

1. Distinguish between true solutions, colloidal solutions, and suspensions as to each of the following, with water as the dispersion medium: size of the dispersed particles, appearance, permanence, ability to diffuse through a membrane. How, theoretically, are these differences accounted for?
2. What is a gel? Give examples.
3. What is an emulsion? Name two factors that must be provided for in order to secure a lasting emulsion and illustrate by reference to some process of cookery or household interest that involves the preparation of an emulsion.
4. a. Is it possible to secure a 50 per cent solution of sodium chloride in either cold or boiling water? Reason.

b. How much sodium chloride must be used per liter of solution if a solution which is saturated at ordinary temperature is required?

c. How much sodium chloride must be used to make a solution of normal concentration?

5. How much sulfuric acid must be used to provide one liter of solution of each of the following: (a) a molar solution, (b) a M/10 solution, (c) a normal solution?

6. Is it possible to secure a solution of mercuric chloride of molar concentration? Of glucose? If so, how much of the solute would be required for two liters of solution? If not, tell why.

7. How much M/10 solution of sodium hydroxide must be used to exactly neutralize 10 cc. of M/10 solution of hydrochloric acid? Explain.

8. Why are solutions on either a molar or a normal basis usually preferred, instead of solutions on a percentage basis, for use in a chemistry laboratory?

9. Under which condition would the blood be capable of holding the higher proportion of oxygen in solution: (a) When the temperature is normal, about 98.6° F.? (b) In a febrile condition as when the temperature is 103° F.? State the reason for your answer.

10. Why would a scald occasioned by the spilling of a boiling solution of brine (concentrated sodium chloride solution) be likely to produce greater tissue injury than a similar scald occasioned by boiling water?

11. Of what advantage is it to the plant that the carbohydrates of its sap (chiefly glucose, fructose, and sucrose) are capable of true solution, whereas the starch found in seeds, roots, or tubers is not capable of true solution?

12. When concentrated brine solutions are emptied on growing grass the plants in the area usually die. What may happen to the root cells that would account for this fact?

13. The membranes of the alimentary canal are normally impermeable to magnesium sulfate. How does the administration of a concentrated solution of this salt affect diffusion in respect to this membrane?

14. a. Assemble in tabulated form contrasting conditions as to true and colloidal solutions with water as dispersing medium, stressing: tendency toward separation of water and dispersed substance; size (diameter) of dispersed particles; behavior as to filtration and diffusion through membranes; boiling and freezing temperatures as compared with those of water alone.

b. Account, theoretically, for all save the last two of these characteristics.

CHAPTER XVII

Acids, Bases, Salts, as Electrolytes. Ionization

In a preceding chapter two of the facts stressed are that acids, bases, and salts must be in water solution when they engage in reactions peculiar to these classes of compounds; and that acids and bases, and the same is true of salts, are of differing chemical activities, depending upon the specific compounds concerned.

ELECTROLYTES AND NON-ELECTROLYTES

Differentiated. Another finding concerning acids, bases, and salts is that they are the only compounds whose water solutions conduct the electric current appreciably; it is for this reason that these compounds have come to be called *electrolytes*. On the other hand, there are compounds whose water solutions do not conduct the electric current appreciably, and these are called *nonelectrolytes*. Among the latter compounds are water itself, all alcohols, and all sugars. Thus:

Hydrochloric acid	are *electrolytes*	Water	are *nonelectrolytes*
Acetic acid	because their	Methyl alcohol	because their
Sodium hydroxide	water solutions	Ethyl alcohol	water solutions do
Ammonium hydroxide	conduct the	Glucose	*not* conduct the
Sodium chloride	electric current	Sucrose	electric current
Cupric sulfate	appreciably.		appreciably.

Conductivity and chemical activity. As for electrolytes, it is found that, providing their solutions are of the same normality, the range of electrical conductivities of said solutions is the same as the range of chemical activities of the specific acids, bases, and salts concerned. The accompanying table illustrates this relationship (p. 238).

In this table the electrolytes are listed from the greatest to the least active chemically, as acids, bases, and salts; but this is also the order of the electrical conductivities of their solutions of the same normality. For the present, the numbers given in connection with these electrolytes will serve only to emphasize the degree of these relationships specified.

Listed in order of chemical activity and conductivity of tenth-normal solution

Hydrochloric acid	.92	Oxalic acid	.50
Nitric acid	92	Copper sulfate	.40
Sodium hydroxide	.91	Zinc sulfate	.40
Potassium hydroxide	.91	Phosphoric acid	.27
N/64 { Barium hydroxide[1]	.92	Tartaric acid	8.5
N/64 { Calcium hydroxide	.90	Acetic acid	1.3
Magnesium hydroxide	—	Ammonium hydroxide	1.3
Potassium chloride	.86	Mercuric chloride	1.0
Sodium chloride	.84	Carbonic acid	.17
Silver nitrate	.81	Hydrosulfuric acid	.07
Sodium nitrate	.79	Boric acid	.01
Barium hydroxide	.77	↓	
Sulfuric acid	.61	Non-electrolytes	

Strong and weak electrolytes. The foregoing leads us to the fact that a *strong electrolyte* is an acid, base, or salt which is very active chemically, and whose water solution conducts the electric current very well; whereas a *weak electrolyte* applies to an acid, base, or salt which is not very active chemically and whose water solution does not conduct the electric current very well.

Nonelectrolytes. There is no sharp line of demarcation between electrolytes and nonelectrolytes since, when weak electrolytes are lined up from the standpoint of their decreasing chemical activities, and decreasing conductivities of their solutions, they merge into nonelectrolytes. Indeed, nonelectrolytes can be regarded as ultra-poor electrolytes. Water, for example, is a typical nonelectrolyte but there are certain phenomena, as we shall see later, which find explanation in the assumption that, after all, water is an electrolyte, although an ultra-poor one.

Electrolytes explained. Because of the phenomena peculiar to electrolytes, chemists long ago came to the conclusion that something very special must happen to acids, bases, and salts when they enter water solution, which bears both on the chemical behavior of these compounds and on the electrical conductivities of their solutions. Furthermore, it seemed likely that, whatever it is that happens, it must take place in differing degrees as to the acids, bases, and salts.

Just what it is that takes place, however, has never been discovered for certain. But along in the 1800's a young Swedish student of chemistry, Svante Arrhenius by name, becoming very much interested in these phenomena, conceived imaginary conditions which, in due time, he and others concluded served fairly satisfactorily to explain most of the factual findings concerned.

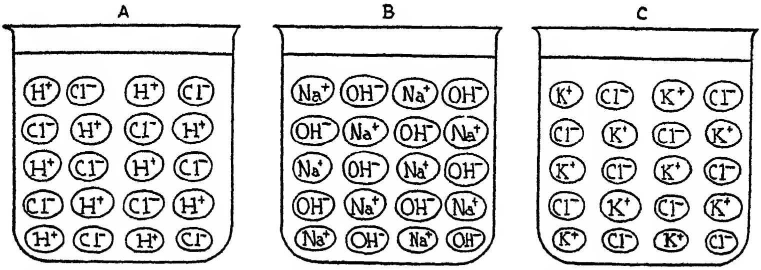
[1] These bases are not sufficiently soluble to make tenth-normal solutions possible.

So, certain of the assumptions of Arrhenius, with modifications of more recent date, will be the subject of our next study.

IONIZATION AND STRONG ELECTROLYTES

First assumption. It is believed that when acids, bases, and salts are in water solution their molecules are dissociated into ions and that these ions participate in chemical reactions as individual substances. Moreover, when *strong electrolytes* are in water solution, it is believed that *all* of their molecules are thus ionized.

Second assumption. Some ions are single atoms, others are groups of atoms in close combination; and all carry electric charges



$HCl \rightarrow H^+ + Cl^-$ Hydrogen ions, Chloride ions — $NaOH \rightarrow Na^+ + OH^-$ Sodium ions, Hydroxyl ions — $KCl \rightarrow K^+ + Cl^-$ Potassium ions, Chloride ions

FIG. 72. Ion molecules are believed to be the only varieties of reacting particles in water solutions of strong electrolytes.

the kind and extent of which is determined by the valences of the atoms and atom groups concerned. It follows, then, from these two assumptions that a solution of hydrochloric acid contains two varieties of reacting particles: hydrogen ions, each of which carries the positive charge of one proton, and chloride ions each of which carries the negative charge of one electron (Fig. 72 A). A solution of sodium hydroxide likewise contains two varieties of particles: sodium ions and hydroxide ions which carry their respective positive and negative charges (Fig. 72 B). And the same is believed to be true of a solution of potassium chloride, the two varieties of ion molecules being potassium ions and chloride ions (Fig. 72 C).

Third assumption. Ion molecules have a tendency to move about in the solution with considerable speed; but this speed is more or less restricted due to the attractive force that must exist between oppositely charged ions. Consequently, in a very concentrated solution of an acid, base, or salt the ions must of necessity be so close to each other and the inter-ion attractive force so great

that their motility is relatively slight. But in a more dilute solution the ions are able to get farther away from each other, thereby effecting a greater freedom of movement (Fig. 73).

Facts explained. We are now in a position to find a fairly satisfactory explanation for certain facts. *First:* Solutions of acids, bases, and salts conduct the electric current because of the ions present, which, due to their electric charges and motilities carry the electric current through the solution; and the extent of the current conductivity depends in part upon the number of ions per unit volume of the solution, but even more upon the *motility of the ions.*

Second: Acids, bases, and salts must be in water solution if they are to engage in chemical reactions that are peculiar to them because, presumably, ions are really the reacting particles concerned, not the undissociated molecules of said acids, bases, and salts; and the rapidity of reactions depends in part upon the concentration of the ions, but more upon the speed with which ions are able to move about in the solution.

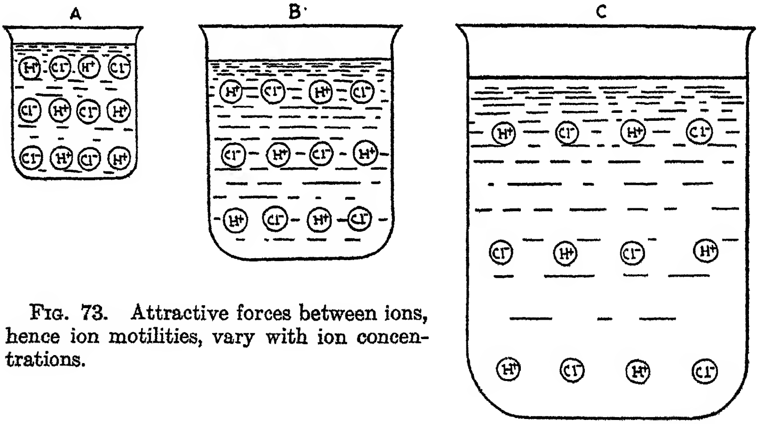


FIG. 73. Attractive forces between ions, hence ion motilities, vary with ion concentrations.

Let these claims be made clearer in the light of examples. Given three solutions of hydrochloric acid as represented in Figure 73 A, B, and C. To begin with, since this acid is in water solution, hydrogen ions and chloride ions are present: ready to conduct the electric current, ready to engage in reactions with other invading molecules. Next, as to the effectiveness of these functions: solution A is exceedingly concentrated, so concentrated that hydrogen ions and chloride ions are so close to each other that their freedom of movement is greatly restricted. As a result, the electric conductivity of the solution is low and the speed of chemical reactions with other ions or molecules is low, since relatively few hydrogen ions

and chloride ions are able to escape from each other in order to make contacts with other reacting particles present.

In solution B, however, while the concentration of ions is decreased, their motilities have increased greatly, hence the ions can carry the electric current more effectively and make more numerous contacts with other molecules in the way of chemical reactions.

But in very dilute solution C, while the ions might even be completely emancipated from inter-ion attractions and their motilities be at maximum speed, they have much longer paths to cover in carrying the electric current across the solution; and from a chemical activity angle, much longer paths to traverse for making contacts with other molecules.

HYDROGEN IONS AND HYDROXYL IONS

Acids as electrolytes and ions common to their solutions. Thus far only strong acids have entered the discussion from the standpoint of their ionization; weak acids will receive consideration in the next chapter. But whether acids are strong or weak, all are believed to be ionized in water solution. And the ions that are common to solutions of all acids are obviously *hydrogen ions;* in fact, one of the definitions of an acid that is frequently given is: *an acid is a substance which is capable of producing hydrogen ions in water solution.*[2]

The partner ions are acid radical ions and they vary with specific acids. Equations for reactions that take place during ionization as to some specific acids are as follows:

$HCl \rightarrow H^+ + Cl^-$ (chloride ions)
$HNO_3 \rightarrow H^+ + NO_3^-$ (nitrate ions)
$HC_2H_3O_2 \rightarrow H^+ + C_2H_3O_2^-$ (acetate ions)
$H_2CO_3 \rightarrow 2\,H^+ + CO_3^{--}$ (carbonate ions)
$H_2SO_4 \rightarrow 2\,H^+ + SO_4^{--}$ (sulfate ions)
$H_3PO_4 \rightarrow 3\,H^+ + PO_4^{---}$ (phosphate ions)

In concentrated solution *

$H_2CO_3 \rightarrow H^+ + HCO_3^-$ (hydrogen carbonate ions)
$H_2SO_4 \rightarrow H^+ + HSO_4^-$ (hydrogen sulfate ions)
$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$ (dihydrogen phosphate ions)
$H_3PO_4 \rightarrow 2\,H^+ + HPO_4^{--}$ (monohydrogen phosphate ions)

* Acids which contain more than one replaceable hydrogen atom are believed to ionize in stages, depending upon the concentration of the acid, in high concentration one or more of the hydrogen atoms remaining in combination with the acid radical. This is believed to be the condition responsible for so-called acid salts such as the sodium hydrogen phosphates, formulas for which are $Na(H_2PO_4)$ and $Na_2(HPO_4)$, and sodium bicarbonate, formula $Na(HCO_3)$ (p. 251).

[2] Since the hydrogen ion carries the positive charge of one proton, the hydrogen atom concerned having parted with its one and only planetary electron, it follows that actually the hydrogen ion is the hydrogen atom nucleus or a single proton. Therefore, another definition of an acid that is favored by some chemists is: *a substance that is capable of producing protons in solution.*

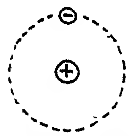
Bases as electrolytes and the common ions. Only strong bases have been considered in the discussion of electrolytes thus far. But regardless of whether bases are strong or weak, all are believed to be ionized in water solution; and the ions that are common to solutions of all bases are *hydroxyl (or hydroxide) ions.* Accordingly, one definition of a base is as follows: *a base is a substance that is capable of producing hydroxyl ions.* The partner ions are metal or ammonium ions and they vary with specific bases. Equations for some of these dissociation reactions are as follows:

$$NaOH \longrightarrow \underset{\text{(Sodium ions)}}{Na^+} + \underset{\text{(Hydroxyl ions)}}{OH^-}$$

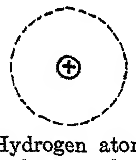
$$Mg(OH)_2 \longrightarrow \underset{\text{(Magnesium ions)}}{Mg^{++}} + 2\,OH^-$$

$$NH_4OH \longrightarrow \underset{\text{(Ammonium ions)}}{NH_4^+} + OH^-$$

Importance of these ions. As for hydrogen ions, also hydroxyl ions, their existence has come to be believed in so thoroughly that they have attained an important place in present-day chemistry. In differing concentrations they are supposed to play their own significant roles in obtaining desired reactions in the laboratory, and in obtaining desired products in manufacturing concerns, and in cookery. They are also believed to play important roles in the health and disease of animals and of plants. We shall, therefore, give some detailed attention to these substances now, with more later.



Hydrogen atom complete, is neutral.



Hydrogen atom without its planetary electron is its positively charged nuclear proton.

FIG. 74

Hydrogen ions. ***Composition.*** *A single hydrogen ion* is an independently reacting particle composed of a single hydrogen atom which, in floating away from the other atom or atoms within the molecule of which it was previously a part, has left its one and only planetary electron in their keeping. This ion, then, carries the charge of the nucleus of the hydrogen atom: namely, that of one proton, or one *ultimate* unit of positive electricity. In other words, a hydrogen ion is an independently reacting proton (Fig. 74).

There are reasons for believing that hydrogen ions do not wander about by themselves, but that each enters into immediate combination with one molecule of water to make what is called an hydronium ion by some, an oxonium ion by others.

$$\underset{\substack{\text{Hydrogen}\\ \text{ion}}}{H^+} + H_2O \longrightarrow \underset{\substack{\text{Hydronium ion}\\ \text{or Oxonium ion}}}{H_3O^+}$$

Relative weight of hydrogen ion molecule. Since the electron which the hydrogen atom leaves behind when it becomes an ion is negligible in weight, the relative weight of a *single hydrogen ion molecule* is that of a single hydrogen atom, or relatively 1.008.

Mole of hydrogen ions. For measuring *large* quantities of hydrogen ions, such as quantities in given solution volumes, the usual gram molecular weight or mole basis is used. But the gram molecular weight of hydrogen ions must be composed of one gram atomic weight (1.008 grams) of hydrogen element carrying one *large* unit of positive electricity; and this weight, as is supposed to be true for *gram molecular weights* of all substances, presumably includes 6.06×10^{23} of the individual hydrogen ions (Fig. 75). We shall need this quantitative data for later use.

H^+

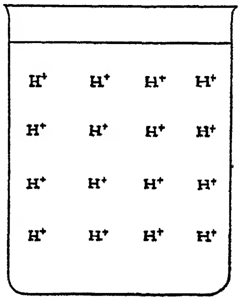
Formula for one hydrogen ion. The ion weighs relatively 1.008 in respect to other molecules.

Each ion carries one *ultimate* unit of positive electricity, meaning the charge of one proton.

H^+

Formula for one molecular weight (1.008) of hydrogen ions which *in grams* is one mole and includes 6.06×10^{23} of these ions.

This weight carries one *large* unit of positive electricity.



6.06×10^{23} hydrogen ions weigh *inclusively* 1.008 grams.

FIG. 75

Hydroxyl ions. ***Composition.*** A *single hydroxyl ion* is an independently reacting particle composed of one hydrogen atom and one oxygen atom in close combination, which have acquired one more electron than belongs to them. The hydroxyl ion, therefore, carries the *ultimate* negative charge of this extra electron.

Relative weight of the hydroxyl ion molecule. Since the extra electron is negligible in weight, the relative weight of the single hydroxyl ion must be the inclusive weight of the oxygen and hydrogen atoms, or relatively 17.008.

Mole of hydroxyl ions. One mole of hydroxyl ions is composed of one gram atomic weight each of oxygen and hydrogen and is therefore 17.008 grams. This weight carries one *large* unit of negative electricity and it includes 6.06×10^{23} of the individual hydroxyl ions (Fig. 76).

OH^-

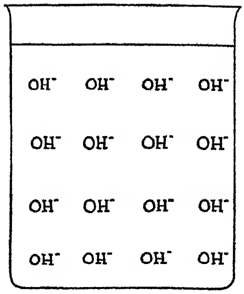
Formula for one hydroxyl ion. The ion weighs relatively 17.008 in respect to other molecules.

Each ion carries one *ultimate* unit of negative electricity, or the charge of one electron.

OH^-

Formula for one molecular weight (17.008) of hydroxyl ions which *in grams* is one mole and includes 6.06×10^{23} of these ions.

This weight carries one *large* unit of negative electricity.



6.06×10^{23} hydroxyl ions weigh *inclusively* 17.008 grams.

FIG. 76

Properties of hydrogen ions. Hydrogen ions are sour. This accounts for the sourness of vinegar, of fruits, of gastric contents, and of other solutions which contain acids, since the acids therein are claimed to have provided hydrogen ions. This is, of course, a *physical property* of this substance. *Chemical properties* of hydrogen ions are believed to be those which are common to solutions of all acids. Some of these are as follows:

Hydrogen ions react with some colored substances. In everyday concerns it is a matter of common knowledge that the careless spattering of salad dressing, or grapefruit juice, or tomato juice frequently leaves a trail of spots on the colored blouse or tie. These spots are believed to be due to a reaction between the colored substances concerned and *hydrogen ions* provided by the acetic acid component of vinegar or the tartaric and other acids of the grapefruit and tomatoes. Attacks of this sort on dyes of clothing are obviously a nuisance; consequently, one of the researches of practical importance to the manufacturer of dyes for such use is to find pigments which are not attacked by hydrogen ions.

But the chemist makes good use of these reactions by selecting substances that are especially sensitive to hydrogen ions in order to detect their presence. Three such substances are blue litmus, yellow methyl orange, and red phenolphthalein, the reactions concerned being, in brief, as follows:

Hydrogen ions + Blue litmus → Red litmus
Hydrogen ions + Yellow methyl orange → Red methyl orange
Hydrogen ions + Red phenolphthalein → Colorless phenolphthalein

Hydrogen ions with tissues and fabrics. Hydrogen ions in high concentration are caustic to tissue cells and fabrics, as is evidenced by the destructive effect produced when solutions of strong acids

are spilled on skin or clothing. Lower concentrations of hydrogen ions in continued contact may be quite irritating to tissues, and fabrics so exposed may be gradually destroyed.

Hydrogen ions with metals above hydrogen. When an acid in water solution is in contact with a *metal above hydrogen*, the reaction which sets in is presumed really to be between the hydrogen ions provided and the metal, to make hydrogen substance and metal ions:

$$\text{Hydrogen ions} + \underset{\text{(above hydrogen)}}{\text{Metal}} \rightarrow \text{Hydrogen} + \text{Metal ions}$$

The acid radical ions present remain unaffected save that they become associated with metal ions made instead of with the previously existing hydrogen ions. Two such reactions are represented thus:

$$2\,H^+ + 2\,Cl^- + Zn^\circ \longrightarrow H_2^\circ + Zn^{++} + 2\,Cl^-$$
$$6\,H^+ + 3\,SO_4^{--} + 2\,Al^\circ \rightarrow 3\,H_2^\circ + 2\,Al^{+++} + 3\,SO_4^{--}$$

Hydrogen ions with hydroxyl ions. When an acid and a base are introduced into the same solution, the hydrogen ions and hydroxyl ions combine to make undissociated water molecules, while the metal ions and acid radical ions become partner ions of the salt product instead of the original acid and base. Here are equations for two such instances:

$$Na^+ + OH^- + H^+ + Cl^- \longrightarrow H_2O + Na^+ + Cl^-$$
$$Ca^{++} + 2\,OH^- + 2\,H^+ + SO_4^{--} \rightarrow 2\,H_2O + Ca^{++} + SO_4^{--}$$

Or representing only the fate of the parties responsible for the reaction and with quantitative data given:

$$H^+ + OH^- \longrightarrow HOH$$

Interpretation. In ultimate terms: one hydrogen ion combines with one hydroxyl ion to make one molecule of water. *In measurable quantities:* one molecular weight of hydrogen ions combines with one molecular weight of hydroxyl ions to make one molecular weight of water. *In gram terms:* 1.008 grams of hydrogen ions combine with 17.008 grams of hydroxyl ions to make 18.016 grams of water.

Properties of hydroxyl ions. The slippery feeling that is characteristic of solutions which contain bases is believed to be the property of hydroxyl ions. The brackish or flat taste experienced when tasting solutions of bases is also attributed to these ions. These are *physical properties* of this substance. The following are *chemical properties* attributed to these ions.

With colored substances. Any attack on a colored substance that is common to all bases in water solution is believed to be due not to the bases themselves but to hydroxyl ions. Certain color changes that take place on the part of dyes of fabrics during launderings are probably due to hydroxyl ions. The salts of soaps hydrolyze to make sodium hydroxide as one product, washing soda likewise hydrolyzes to make this base, which in turn dissociates to make *hydroxyl ions.* The latter are in *low concentration* to be sure, since not very much sodium hydroxide is made in these reactions (p. 183); but nonetheless the hydroxyl ions may be present in sufficient concentration to react appreciably with dyes that are sensitive to their attack:

Soap

Sodium stearate + Water ⟶ Sodium hydroxide + Stearic acid
Sodium palmitate + Water ⟶ Sodium hydroxide + Palmitic acid
Sodium oleate + Water ⟶ Sodium hydroxide + Oleic acid
↓
Hydroxyl ions + Sodium ions

Washing soda

Sodium carbonate + Water ⟶ Sodium hydroxide + Carbonic acid
↓
Hydroxyl ions + Sodium ions

Household ammonia

Ammonium hydroxide ⟶ *Hydroxyl ions* + Ammonium ions

But the chemist makes good use of these reactions of hydroxyl ions with pigments to detect their presence. For this purpose such colored substances are selected as are especially sensitive to reaction with these ions; three of these are red litmus, red methyl orange, and colorless phenolphthalein; and they react with hydroxyl ions with results stated briefly as follows:

Hydroxyl ions + Red litmus → Blue litmus
Hydroxyl ions + Red methyl orange → Yellow methyl orange
Hydroxyl ions + Colorless phenolphthalein → Red phenolphthalein

With proteins. Hydroxyl ions attack proteins of animal tissues. When dishes or clothes are cleansed in water to which such softening agents as sodium carbonate or sodium phosphate have been added, the hands become rough because of the reaction between proteins of the skin and hydroxyl ions obtained after the manner just previously presented (p. 180). If silks or woolens, which are mainly protein, are soaked in washing soda solution, their fibers are weakened through attacks presumed to be due to these ions.

Naturally the higher the concentration of hydroxyl ions the more marked the attack becomes (Fig. 77). Consequently, such high concentrations of hydroxyl ions as are obtainable directly from the soluble and strong bases, sodium and potassium hydroxides,

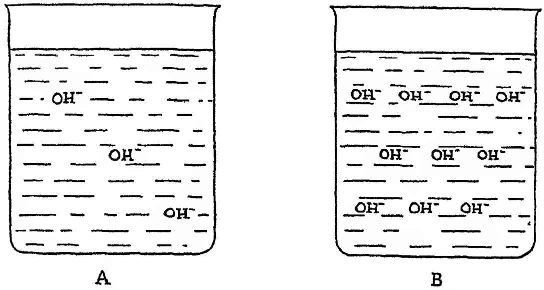


FIG. 77. Because of the higher concentration of hydroxyl ions all reactions with this substance will be more marked in solution B than in solution A.

can produce very disastrous results with proteins; hence the labels caustic soda and caustic potash which are applied to these bases.

How decrease the concentration of hydrogen or hydroxyl ions. Since these ions combine with each other to make undissociated water, it becomes obvious that an excellent method for decreasing the concentration (1) of hydrogen ions is to add hydroxyl ions (Fig. 78) and (2) of hydroxyl ions to add hydrogen ions (Fig. 79). Should it be desired to get rid of the effect of hydrogen ions or of

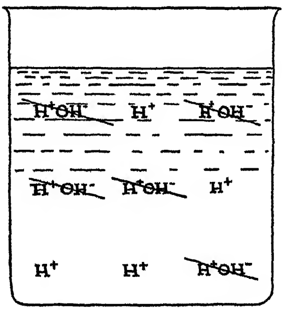


FIG. 78. To Decrease the Concentration of Hydrogen Ions

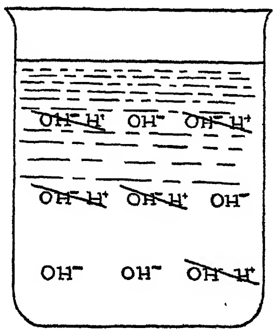


FIG. 79. To Decrease Concentration of Hydroxyl Ions

hydroxyl ions entirely, then an equal number of hydroxyl ions or of hydrogen ions must be added respectively. Should it be important that no *excess* of either of these ions be obtained within the solution, then exact quantitative procedures with skilled technic must be employed.

Treatment of injuries due to these ions. Injuries that result from the accidental spilling or spattering of acids or bases on either tissues or fabrics are presumably caused by the action of hydrogen ions in the case of acids, or hydroxyl ions in the case of bases. Therefore, the principle involved in dealing with these accidents is to limit the extent of the injury by promptly *reducing the concentration of the destructive ions.*

When the injury is due to hydrogen ions the treatment may vary, but in general it should consist of the following procedures: *first,* flush the area thoroughly with an abundant flow of water, thus washing away some of the hydrogen ions and decreasing the concentration of the remaining portion by dilution; *second,* apply a solution which will supply hydroxyl ions, in safe concentration, to combine with hydrogen ions to make harmless water (Fig. 78). The selection of a suitable source of hydroxyl ions becomes a matter of importance. For the treatment of fabrics attacked by hydrogen ions a solution of ammonium hydroxide may be used, this being a weak base, hence capable of producing hydroxyl ions only in relatively low concentration (p. 252):

An acid which yields a destructively high concentration of hydrogen ions.................... $HCl \longrightarrow H^+ + Cl^-$

A weak base which yields hydroxyl ions in safe concentration to get rid of hydrogen ions........ $NH_4OH \longrightarrow OH^- + NH_4^+$

$$\downarrow$$

$$H_2O$$

Both hydrogen ions and hydroxyl ions are removed from the system to make water (a nonelectrolyte).

For getting rid of hydrogen ions on the skin or mucous membranes, lime water, a solution of calcium hydroxide, is sometimes used, since this base, although strong and therefore an excellent source of hydroxyl ions, is only very slightly soluble in water, hence can provide only a low concentration of hydroxyl ions. Still another good source of a low concentration of hydroxyl ions is provided by solutions of some salts after the order of sodium carbonate, sodium bicarbonate, and potassium phosphate. It will be recalled that such sources provide only dilute solutions of these excellent bases, hence only relatively low concentrations of hydroxyl ions.

When the injurious agent is hydroxyl ions the treatment should include: *first,* a thorough flushing with water, if possible; *second,* the application of a suitable acid in order to secure hydrogen ions

for combining with the hydroxyl ions to make water (Fig. 79). And it is well to select a *weak* acid for this purpose in order to obtain the desired hydrogen ions, but in low concentration. Vinegar, which provides acetic acid, or lemon juice, which provides several weak acids, citric acid among them, are commonly advised for this purpose:

A base which yields hydroxyl ions in sufficiently *high concentration to be caustic* in effect .... $NaOH \longrightarrow OH^- + Na^+$

A weak acid used to provide the desired hydrogen ions as an antidote.................. $HC_2H_3O_2 \longrightarrow H^+ + C_2H_3O_2^-$

$\downarrow$

Thus the concentration of the injurious agent, the hydroxyl ions, is reduced........................ H_2O

A nonelectrolyte

Boric acid, although a very weak electrolyte, yields enough hydrogen ions, if used freely, to be effective in reducing the concentration of hydroxyl ions, and is frequently employed for the treatment of sensitive tissues, such as the conjunctiva of the eye.

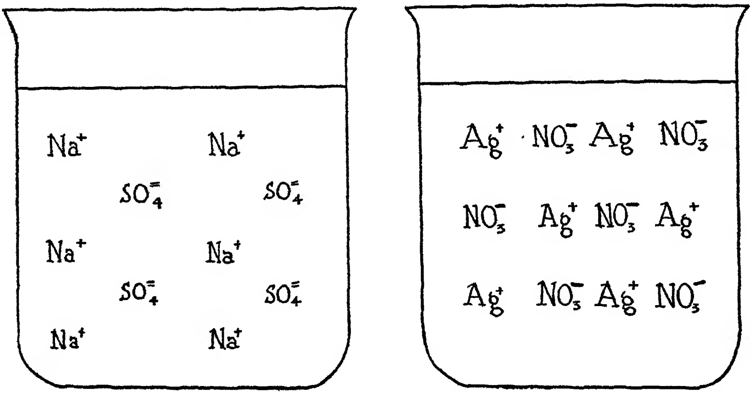
SALTS AS ELECTROLYTES

As strong electrolytes. Nearly all salts are strong electrolytes, hence in water solution the salt molecules are believed to be one hundred per cent ionized, the ions concerned being metal ions or ammonium ions and acid radical ions. Equations for some of these ionization reactions as to salts are as follows:

$$NaCl \longrightarrow Na^+ + Cl^-$$
$$KCl \longrightarrow K^+ + Cl^-$$
$$Na_2SO_4 \longrightarrow 2\ Na^+ + SO_4^{--}$$
$$CuSO_4 \longrightarrow Cu^{++} + SO_4^{--}$$
$$NH_4NO_3 \longrightarrow NH_4^+ + NO_3^-$$

Ions are active agents. Just as ions obtained from acids and bases are really the active agents, so these ions obtained from salts, not the undissociated salt molecules, are presumably the substances that participate in chemical reactions and in conducting the electric current. And the same conditions apply as to efficacy of salt ions as apply for all ions: namely, the speed with which these ions engage in chemical reactions and the speed with which they carry the electric current through the solution depends in part upon the concentration of the ions, but even more upon their degree of motility (p. 240).

No common ions. *There is no one ion substance that is supplied by all salts* in water solution. To be sure metal ions and acid radical ions must be present within solutions of all salts, but there can be different metal ions and different acid radical ions. Representations of substances obtained within solutions of sodium sulfate and silver nitrate are given in Figure 80.



Reacting particles are:
Sodium ions
Sulfate ions

Reacting particles are:
Silver ions
Nitrate ions

FIG. 80. Salts dissociate in water solution to make metal ions and acid radical ions.

Normal salts and acid salts. Most salts are *normal salts* in that they have as constituents only metal radicals and acid radicals. All salts discussed in the foregoing are of this order. But there are some salts, called *acid salts*, in which part of the hydrogen radical, originally in the acid from which the salt was made, remains in more or less close combination with the acid radical, and as long as this combination persists this hydrogen constitutes a part of the acid radical. One such salt is the familiar sodium bicarbonate which is used in cookery and to some extent in medical practice and which is very important physiologically; others are the sodium and potassium hydrogen salts of phosphoric acid, which are also of considerable physiological importance (p. 503):

Sodium bicarbonate	$NaHCO_3$
Sodium monohydrogen phosphate	Na_2HPO_4
Potassium monohydrogen phosphate	K_2HPO_4
Sodium dihydrogen phosphate	NaH_2PO_4
Potassium dihydrogen phosphate	KH_2PO_4

Since the above is *known* to be the composition of such salts it is logical to conclude that within their water solutions, while the positively charged ions are metal ions, the negative ions contain the hydrogen atoms as part of said ions. The following equations represent reactions that are believed to take place when some of the above-mentioned salts dissociate in water solution (p. 241):

$$NaHCO_3 \rightarrow Na^+ + HCO_3^-$$
$$NaH_2PO_4 \rightarrow Na^+ + H_2PO_4^-$$
$$K_2HPO_4 \rightarrow 2\,K^+ + HPO_4^{--}$$

Physiological aspects of acids, bases, and salts as electrolytes are presented in Chapter XXXI.

Questions

1. What is an electrolyte? What substances, in general, behave thus? Differentiate between strong electrolytes, weak electrolytes, and nonelectrolytes. Give examples.

2. What are the basic assumptions of the ionization theory that are stressed in this chapter?

3. a. From the standpoint of the ionization theory what are the following: (1) an acid, (2) a base, (3) a hydrogen ion, and (4) a hydroxyl ion?
   b. To what are the properties that are common to solutions of all acids supposedly due? The properties common to solutions of all bases?

4. Upon what two conditions does the chemical activity of ions within a solution depend? Give examples.

5. Solutions of hydrogen ions are frequently caustic to tissues and fabrics. What would you do to diminish such an injury should a few drops of a strong acid solution accidentally become spattered on your hand? On your clothing? State the reason for each step in your procedure.

6. How would you proceed to reduce the concentration of hydrogen ions in a solution? (Two methods)

7. Why is it important that a sink drain be thoroughly flushed with water after disposing of any strong acid?

8. Why is a solution of potassium hydroxide capable of producing a destructive effect on tissues or fabrics?

9. Sodium and potassium hydroxides should be stored in locations where neither children nor careless persons will accidentally come in contact with them. Why is this an important precaution? From what sources can safe concentrations of hydroxyl ions be secured for ordinary household purposes?

10. State why each of the following can function as an indirect source of hydroxyl ions: lime water, milk of magnesia, sodium bicarbonate, calcium oxide, soap. Represent by equations the reactions involved in each case to provide the hydroxyl ions.

CHAPTER XVIII

Weak Electrolytes. Equilibrium. Water as an Electrolyte

The discussion of ionization in the foregoing chapter was in respect only to *strong* electrolytes, which, it must be borne in mind, are completely ionized in water solution with two varieties of reacting particles present: namely, the two varieties of ions. Conditions are believed to be different with weak electrolytes.

Weak electrolytes not completely ionized. When a weak acid, base, or salt enters water solution, only part, and always less than half, of the molecules are presumed to dissociate to make ions.

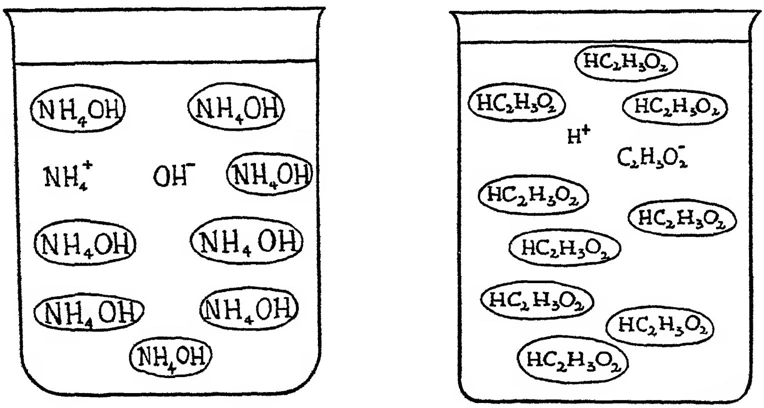


FIG. 81

It follows, therefore, that within a solution of a weak electrolyte there are *three* kinds of reacting particles: the two varieties of ion molecules and the undissociated molecules of the acid, base, or salt, with the undissociated molecules in predominance. Examples are given in Figure 81.

Two opposing reactions with an aim to establish equilibrium. When a weak electrolyte enters solution the dissociation to make ions becomes accompanied presently by a combination between ions to remake some of the undissociated molecules of the acid, base, or salt. As a result, two opposing reactions are continuously taking place. Moreover, these two reactions are aiming continu-

ously to establish a condition of equilibrium, that is, a condition in which the speed of dissociation, or the number of molecules that ionize during any given time, is equal to the speed of association, or the number of combinations between ions to remake undissociated molecules. For example:

In the solution of acetic acid represented in Figure 81 two reactions are taking place: acetic acid molecules are dissociating to make hydrogen ions and acetate ions, and at the same time some of these ions are combining to remake undissociated molecules of acetic acid. When this acid first enters solution the reaction to make ions is the speedier, but as more and more ions are made this first reaction speeds down and combinations between ions speed up; consequently, if let alone, the time will come, and soon, when the two reactions will be equal in speed and the desired condition of equilibrium attained.

The same reasoning holds for the two reactions in the solution of ammonium hydroxide (Fig. 81).

Relationship between concentrations of unionized and ionized portions of weak electrolytes. From certain experimental findings as to properties of weak acids, bases, and salts in water solution, there is reason to believe that when the two reactions are at equilibrium, the concentration of the unionized portion is always greater than that of the ionized portion. This is exemplified diagrammatically in Figure 81 and again in the following equations which represent the two-way reactions concerned and which make use of arrows of differing lengths for indicating different concentrations of substances as to each other on the two sides of the reactions:

$$HC_2H_3O_2 \leftrightarrows H^+ + C_2H_3O_2^-$$
$$NH_4OH \leftrightarrows NH_4^+ + OH^-$$
$$HgCl_2 \leftrightarrows Hg^{++} + 2\ Cl^-$$

Interpretation of second expression. Two reactions are taking place: ionization to make ammonium ions and hydroxyl ions and combination between these ions to make undissociated molecules of ammonium hydroxide. When these two reactions are at equilibrium there is a higher concentration of undissociated molecules of ammonium hydroxide than of ammonium and hydroxyl ions.

Aside from this relationship that must always be met between ionized and unionized portions of weak electrolytes, the exact concentrations as to these portions differ with each electrolyte and with the concentration of the acid, base, or salt as a whole. For example:

As to acetic acid

In .1 normal solution the two reactions are at equilibrium when:

$$\underset{\substack{98.7\% \text{ of the acetic}\\ \text{acid is unionized}}}{HC_2H_3O_2} \rightleftarrows \underbrace{H^+ + C_2H_3O_2^-}_{\substack{1.3\% \text{ continues}\\ \text{to be ionized}}}$$

In normal solution the two reactions are at equilibrium when:

$$\underset{\substack{99.6\% \text{ of acetic acid}\\ \text{is unionized}}}{HC_2H_3O_2} \rightleftarrows \underbrace{H^+ + C_2H_3O_2^-}_{.4\% \text{ is ionized}}$$

As to phosphoric acid

In .1 normal solutions the two reactions are at equilibrium when:

$$\underset{\substack{73\% \text{ of this acid continues}\\ \text{to be unionized}}}{H_3PO_4} \rightleftarrows \underbrace{H^+ + H_2PO_4^-}_{27\% \text{ is ionized}}$$

In tenth normal solution of phosphoric acid only the "first hydrogen" separates to make ions, the rest of the hydrogen remains in combination in the dihydrogen phosphate ion (p. 241).

Facts explained. The theoretical explanation as to why weak acids, bases, and salts are not very active chemically and why their solutions are poor conductors of the electric current is obvious, since, according to belief, it is because the concentrations of their ions, as the active agents, are of necessity very low. And, of course, the extent of their weakness must depend upon the extent to which they dissociate to make ions. Thus, in tenth normal solution, phosphoric acid with 27 per cent dissociation is more active than acetic acid with 1.3 per cent dissociation, just as acetic acid, in turn, is more active than boric acid with .01 per cent dissociation into ions.

Herein, therefore, lies the explanation as to why it is relatively safe to have weak acids and weak bases around without taking precautionary measures for protection against carelessness, and why it is safe to use such acids and bases more or less freely, since it is impossible to obtain high concentrations of hydrogen ions or hydroxyl ions from them.

Response to a disturbing factor. When equilibrium is once obtained on the part of a weak electrolyte, this condition of two opposing reactions taking place at equal speeds persists indefinitely until a disturbing factor enters the field. Some of these are as follows:

1. *If any water is removed* by evaporation, thereby rendering the electrolyte more concentrated, although both reactions continue to take place, the speed of combination between ions becomes favored over the speed of dissociation, and will continue to be thus favored as long as the evaporation persists. The reason, of course, is that with an increase in the concentration of the acid, base, or salt as a whole there must be an increase in its unionized portion

in relation to the ionized portion when the two reactions are at equilibrium.

2. *If more water is added,* thus diluting the electrolyte, the speed of dissociation or ionization becomes favored over that of ion combination (why?) until the dilution is discontinued and equilibrium between the two reactions is again established.

3. *If one of the ion substances is removed,* again, the ionization reaction will be favored over the combinations between ions as long as ion removal continues. For example:

Given a solution in which two reactions as to ammonium hydroxide are at equilibrium. Upon introducing hydrogen ions this equilibrium will be disturbed due to the removal of hydroxyl ions since they will begin to combine with these hydrogen ions to make undissociated molecules of water. Hence the reaction in the direction of the ionization of ammonium hydroxide will be favored over the reverse reaction as long as this disturbance continues.

$$\begin{array}{lcl} NH_4OH & \rightleftarrows & NH_4^+ + \begin{array}{c} OH^- \\ H^+ \\ \downarrow \\ H_2O \end{array} \end{array}$$

4. On the other hand, *if one of the ion substances is added to the solution* from another electrolyte without adding any of the partner ion, combination between the ions will be favored over the dissociation reaction as long as this disturbing factor is present. Thus:

Again, given a solution of ammonium hydroxide in which the two reactions have attained equilibrium. If ammonium ions are introduced, from an ammonium salt, without introducing hydroxyl ions also, from that instant the

$$\begin{array}{c} \text{Ammonium ions introduced} \\ \text{from another source} \\ \downarrow \\ NH_4OH \rightleftarrows NH_4^+ + OH^- \end{array}$$

equilibrium is disturbed, since combination between ammonium and hydroxyl ions will be favored over the dissociation reaction. And this disturbance of the equilibrium as to ammonium hydroxide will persist as long as ammonium ions continue to be introduced from another soufce than ammonium hydroxide itself.

In general, as to any weak electrolyte aiming at equilibrium in the presence of some disturbing factor, nature favors the one of the two reactions — dissociation to make ions or combination between ions — which renders the greater aid in restoring the desired equilibrium condition.

Relative concentrations of the two ions. It is believed that the relative concentrations of the two ion substances can vary in respect to each other and still have the two reactions as to the

electrolyte at equilibrium in each instance. Let us consider various possibilities in the light of definite examples:

In regard to phosphoric acid

1. As indicated in the following equation, if phosphoric acid is the only electrolyte present in the solution, always the concentration of the hydrogen ions will be maintained at three times that of the phosphate ions, since three hydrogen ions are made for every one phosphate ion:

$$H_3PO_4 \rightleftarrows 3\,H^+ + PO_4^{---}$$

But should hydroxyl ions from another electrolyte be introduced, they will immediately combine with some of the hydrogen ions present to make water molecules, and as long as this disturbance continues the forward reaction is favored with the making of more and more phosphate ions. As a result, when this disturbance ceases, providing hydrogen ions are still present, the two

$$\begin{array}{cccc} H_3PO_4 \rightleftarrows & 3\,H^+ & + & \Large PO_4^{---} \\ & 3\,OH^- & & \\ & \downarrow & & \\ & 3\,H_2O & & \end{array}$$

reactions as to phosphoric acid will again attain equilibrium but in the presence of a higher concentration of phosphate ions than of hydrogen ions.

2. On the other hand, should calcium ions be introduced they will combine with phosphate ions to make insoluble calcium phosphate, and again the forward reaction will be favored as long as this introduction of calcium ions continues. Then when the disturbance is ended and the two reactions as to phosphoric acid are again at equilibrium the concentration of the hydrogen ions will be even more than three times greater than that of the phosphate ions:

$$\begin{array}{cccl} 2\,H_3PO_4 \rightleftarrows & 6\,\Large H^+ & + & 2\,PO_4^{---} \\ & & & 3\,Ca^{++} \\ & & & \downarrow \\ & & & Ca_3(PO_4)_2 \downarrow \text{Precipitated} \end{array}$$

In regard to acetic acid

1. As is indicated in the following equation, when the two reactions as to acetic acid are at equilibrium the concentrations of the hydrogen ions and acetate ions are equal — providing acetic acid is the only source of these ions:

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-$$

2. But if hydroxyl ions are introduced from a base the ionization reaction as to acetic acid will begin to be favored over ion combinations due to the removal of hydrogen ions to make water molecules. Then when the disturbance ceases and the two reactions as to acetic acid are again at equilibrium, the concentration of the acetate ions will be greater than that of the hydrogen ions:

$$\begin{array}{cccc} HC_2H_3O_2 \rightleftarrows & H^+ & + & \Large C_2H_3O_2^- \\ & OH^- & & \\ & \downarrow & & \\ & H_2O & & \end{array}$$

3. But if another acid is introduced so that more hydrogen ions are added

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-$$

$$HCl \longrightarrow H^+ + Cl^-$$

to the solution than those provided by acetic acid, but no other source of acetate ions, then when the two reactions as to acetic acid are again at equilibrium the concentration of hydrogen ions will be greater than that of acetate ions.

Conclusion. So it is that there is no set concentration relationship as to the two varieties of ions contributing to a weak electrolyte when its two reactions are at equilibrium: (1) under one set of circumstances the concentration of one of the contributing ions can be relatively high and the other ions low as to concentration; (2) under other conditions the reverse can be the situation; (3) and under still other circumstances the concentrations of the two contributing ions can be equal. But under all conditions, it must be remembered, always the concentration of the undissociated portion of the weak acid, base, or salt is relatively high.

Practical issues attendant upon the aim of weak electrolytes to attain equilibrium. This aim on the part of weak electrolytes to attain equilibrium as to their two reactions and their sensitiveness to disturbances play an important part in securing desired reactions in the laboratory and elsewhere; they also have physiological significance.

Within the blood there are ions that are provided by various strong acids, bases, and salts, and as strong electrolytes, they are believed to be completely ionized. But most of the acid components of the blood are weak. Carbonic acid, lactic acid, phosphoric acid, and fatty acids are always present; and, since these are *weak* electrolytes two reactions are always taking place as to every one of them with an aim to establish a condition of equilibrium. However, when one considers some of the disturbing factors that are continuously in operation: (1) the entrance of some of these ions and their undissociated molecules from the intestine; (2) absorption and return of all of them through membranes to and from the lymph and cells; (3) the removal of these ions and their undissociated molecules at the kidneys, some to be returned in part, some not — when one considers all of these disturbing factors, one is led to wonder whether weak electrolytes in the blood (or lymph, or cells) ever do accomplish their desired equilibria. And probably they do not, save perhaps transiently. Indeed, it is quite possible that should all weak electrolytes in these locations

ever attain their mutual equilibria, the animal would be a dead animal and not a living one.

WATER AS AN ELECTROLYTE

Heretofore water has been regarded only as the medium in which ionic dissociation takes place. But the time has come for considering the belief that, even though *one* acid, or base, or salt, or even though *several* or *many* acids, bases, and salts may be present, water itself as a weak electrolyte is aiming at establishing an equilibrium condition on the part of its two reactions: namely, dissociation to make hydrogen ions and hydroxyl ions, and combination between these ions to make undissociated water molecules.

Concentrations at equilibrium. Since water is an ultra-poor electrolyte, when the desired equilibrium condition is obtained, it must be in the presence of a *relatively ultra-high concentration of the unionized water and a relatively ultra-low concentration of the ionized portion of the water,* a condition represented thus:

$$H_2O \xleftarrow[\rightarrow]{\qquad} H^+ + OH^-$$

Hydrogen ion and hydroxyl ion concentrations in relation to each other. In regard to the concentrations of hydrogen ions and hydroxyl ions within the ionized portion of water, as is the case with the two ion substances of other electrolytes, *these can vary as to each other* and still have the several water systems at equilibrium. But before going into this further let us turn to the measurements used for these ion concentrations.

Basis for measuring these concentrations and their shorthand representations. Hydrogen and hydroxyl ions are measured in terms of *molar quantities* (p. 226) of these two substances *in one liter of the solution*, and the adopted shorthand characters that have come to be used in this connection are cH and cOH. For example, within given solutions:

cH = .25, means that 1 liter of solution contains .25 mole of hydrogen ions.
cH = .001, means that 1 liter of solution contains .001 mole of hydrogen ions.
cOH = .125, means that 1 liter of solution contains .125 mole of hydroxyl ions.
cOH = .0003, means that 1 liter of solution contains .0003 mole of hydroxyl ions.

With this information we are ready for the condition that must be met on the part of hydrogen ion and hydroxyl ion concentrations, since, on the mole-per-liter basis — and taking advantage of

the shorthand devices presented above — the two reactions on the part of water, as an electrolyte, are at equilibrium whenever

$$cH \times cOH = .00000000000001 \text{ or } 10^{-14}$$

This, translated, means that the two reactions as to water are at equilibrium when the molar concentration of hydrogen ions multiplied by the molar concentration of hydroxyl ions, in one liter of the solution, is equal to this exceedingly small value of 10^{-14}. Consequently, regardless of whether concentrations of hydrogen ions and hydroxyl ions are equal, or whether the concentration of hydrogen ions is greater than that of hydroxyl ions, or vice versa, if this relationship is obtained the two reactions as to the water system are at equilibrium. For example:

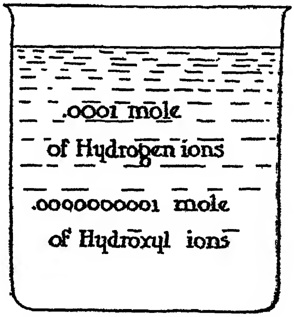
1. If within a given solution (Fig. 82)

   $cH = .0001 \text{ or } 10^{-4}$

   $cOH = .0000000001 \text{ or } 10^{-10}$

   the water, as an electrolyte, is at equilibrium since

10^{-4}	$\times$ 10^{-10}	$= 10^{-14}$
mole of hydrogen ions	mole of hydroxyl ions	



One liter of solution

FIG. 82

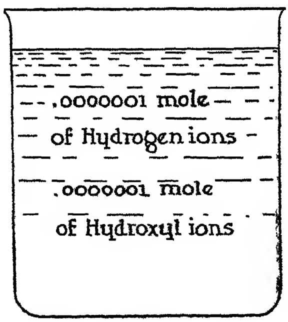
2. If within another solution (Fig. 83)

   $cH = .0000001 \text{ or } 10^{-7}$

   $cOH = .0000001 \text{ or } 10^{-7}$

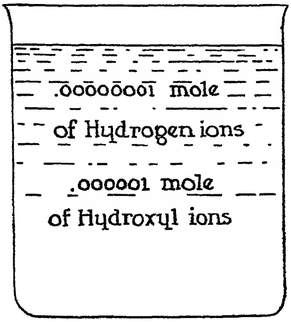
   the water system is likewise at equilibrium since

10^{-7}	$\times$ 10^{-7}	$= 10^{-14}$
mole of hydrogen ions	mole of hydroxyl ions	



One liter of solution

FIG. 83



One liter of solution

FIG. 84

3. If within still another solution (Fig. 84)

cH $= .00000001$ or 10^{-8}

cOH $= .000001$ or 10^{-6}

water, as an electrolyte, is again at equilibrium since

10^{-8}	$\times$	10^{-6}	$=$	10^{-14}
mole of hydrogen ions		mole of hydroxyl ions		

Or more briefly put in respect to the following *thirteen solutions:*

a. when cH = .1 or 10^{-1}.............and cOH = .0000000000001 or 10^{-13}
b. when cH = .01 or 10^{-2}............and cOH = .000000000001 or 10^{-12}
c. when cH = .001 or 10^{-3}...........and cOH = .00000000001 or 10^{-11}
d. when cH = .0001 or 10^{-4}..........and cOH = .0000000001 or 10^{-10}
e. when cH = .00001 or 10^{-5}.........and cOH = .000000001 or 10^{-9}
f. when cH = .000001 or 10^{-6}........and cOH = .00000001 or 10^{-8}
g. when cH = .0000001 or 10^{-7}.......and cOH = .0000001 or 10^{-7}
h. when cH = .00000001 or 10^{-8}......and cOH = .000001 or 10^{-6}
i. when cH = .000000001 or 10^{-9}.....and cOH = .00001 or 10^{-5}
j. when cH = .0000000001 or 10^{-10}...and cOH = .0001 or 10^{-4}
k. when cH = .00000000001 or 10^{-11}...and cOH = .001 or 10^{-3}
l. when cH = .000000000001 or 10^{-12}..and cOH = .01 or 10^{-2}
m. when cH = .0000000000001 or 10^{-13} and cOH = .1 or 10^{-1}

then in each instance the water, as an electrolyte, is at equilibrium, since in each solution cH $\times$ cOH $= 10^{-14}$. And there can be various molar concentrations of hydrogen ions and hydroxyl ions between these whole-number negative-power-of-ten values. Thus, when within the solution concerned,

cH $= 10^{-3.2}$ and cOH $= 10^{-10.8}$ the water system is at equilibrium.
cH $= 10^{-8.7}$ and cOH $= 10^{-5.3}$ the water system is at equilibrium.

cH and cOH and the reaction of the solution. ***Solutions neutral in reaction.*** Obviously it is only when within the solution concerned there are present .0000001 mole of hydrogen ions and .0000001 mole of hydroxyl ions per liter, or when the cH of the solution is 10^{-7} and the cOH is likewise 10^{-7}, that *the solution is neutral in reaction.* (Figure 83, also solution g in above tabulation.) This is always the case if water is the only electrolyte present since, when obtained from water itself, hydrogen ions and hydroxyl

ions are made in equal numbers as represented in the following equation:

$$H_2O \rightarrow H^+ + OH^-$$

But a solution can also contain such proportions of acids, bases, and selected salts that all of them, together with the water, will attain their several equilibria in the presence of equal concentrations of hydrogen ions and hydroxyl ions.

Solutions acid in reaction. Solutions are acid in reaction when cH values within the same are from ever so slightly above 10^{-7} moles of hydrogen ions up through 10^{-1} moles per liter, and the corresponding cOH values are from ever so slightly below 10^{-7} down through 10^{-13} moles per liter. As examples, solutions **f**, **e**, **d**, **c**, **b**, and **a** in the foregoing tabulation are acid in reaction. But in such solutions an acid, or acids, must be present along with the water, since the concentration of hydrogen ions is greater than that of hydroxyl ions, or in shorthand language, the *cH of the solution is greater than its cOH*. But so also may bases and salts, hence their ions, be present.

Solutions basic in reaction. Solutions are basic in reaction in which cH values are ever so slightly below 10^{-7} moles down through 10^{-13} moles per liter, whereas the corresponding cOH values are from ever so slightly above 10^{-7} moles per liter up through 10^{-1} moles per liter. As examples, solutions **h**, **i**, **j**, **k**, **l**, and **m** in the foregoing tabulation are basic in reaction. In such solutions a base, or bases, must be present along with the water, since the *concentration of hydroxyl ions is greater than that of hydrogen ions*. But so also may acids and salts and their ions be present as well as other substances.

Necessary to specify only the cH or the cOH of the solution. For those who understand that this fixed relationship between the concentrations of hydrogen ions and hydroxyl ions must be met on the part of water at equilibrium, it is necessary to specify *only* the cH, or *only* the cOH, of the solution, regardless of whether said solution is acid, basic, or neutral in reaction, since a given molar concentration of hydrogen ions, or the cH of a solution, means automatically a definite molar concentration of hydroxyl ions, or a definite cOH within the solution. For example:

1. If the cH of the solution is 10^{-5} or .00001 mole of hydrogen ions in 1 liter of solution,	then it follows that the cOH of the solution must be 10^{-9} or .000000001 mole of hydroxyl ions per liter of solution.

2. If the cH of the solution is $10^{-2.3}$ or between .01 and .001 mole of hydrogen ions in 1 liter of solution,	then the cOH of the solution must of necessity be $10^{-11.7}$ or between 10^{-11} and 10^{-12} mole of hydroxyl ions in 1 liter of the solution.
3. If the cH of a solution is 10^{-8} or .00000001 mole of hydrogen ions in 1 liter of solution,	then the cOH must be 10^{-6} or .000001 mole of hydroxyl ions in 1 liter of solution.

Shorthand notations for cH values. Since, many times, molar concentrations of hydrogen ions are for convenience recorded on the basis of ten lowered to appropriate negative powers, chemists have adopted the practice of representing these values simply by the power notations concerned. The label given to such a notation is pH.[1] Thus:

	pH notations
cH = 10^{-1}	pH 1
cH = $10^{-1.5}$	pH 1.5
cH = 10^{-2}	pH 2
cH = 10^{-3}	pH 3
cH = $10^{-3.7}$	pH 3.7
cH = 10^{-8}	pH 8
cH = $10^{-8.6}$	pH 8.6
cH = 10^{-9}	pH 9
etc.	etc.

1. pH 2 is the shorthand notation which means that within the solution the cH = 10^{-2} and the cOH = 10^{-12}.

2. pH 3.7 is the shorthand notation which means that within the solution the cH = $10^{-3.7}$ and the cOH = $10^{-10.3}$

3. pH 8 means that the cH of the solution is 10^{-8} and the cOH is 10^{-6}.

4. pH 8.6 means that the cH of the solution is $10^{-8.6}$ and the cOH is $10^{-5.4}$.

There are those who confuse these pH notations with the cH values which they represent. This signifies a lack of real understanding of the relationship between these convenient expressions.

Importance of hydrogen ion and hydroxyl ion concentrations in various concerns. Findings as to the practical significance of these concentrations are of very recent date. Indeed, it is only a matter of perhaps about twenty years since discoveries began to be made that hydrogen ion and hydroxyl ion concentrations within solutions constitute a very important factor in securing desired, or undesired, results in various concerns.

[1] In this text pH notations are defined as the negative powers on a basis of 10 (or the negative logarithms) of the cH values of solutions. More frequently, however, pH is defined as the positive power on a basis of 10 (or the positive logarithm) of the reciprocal of the cH of the solution. But the pH value under either definition is the same. Thus:

$$\text{cH} = 10^{-5}\ldots\ldots\ldots\ldots\text{pH} = 5$$

$$\frac{1}{\text{cH}} = \frac{1}{10^{-5}} = 10^{5}\ldots\ldots\text{pH} = 5$$

The reason for the more usual concept is that computations for most cH values of solutions are more readily made from figures given on the basis of 10 to positive powers than from figures on the basis of 10 to negative powers. Therefore, the computation is made in terms of the reciprocal of the cH of the solution, then converted to the actual cH value.

It is well known, now, that the hydrogen ion concentration of the medium helps to determine the *exact color and shade of the specific dye*. The electro-chemist has learned that the hydrogen ion concentration of the solution in contact with a metal is one factor which determines the extent of *corrosion;* also that the concentration of hydrogen ions must be reckoned with in the *effectiveness of metal electroplating*. Sanitary engineers have discovered that hydrogen ion concentration is a factor to be considered in *effective water purification and sewage disposal.*

Food chemists of these days know that the hydrogen ion concentration of bread dough is one condition which determines the *length of the fermentation period* — whether it is too long, too short, or just right, consequently whether the finished loaf will be light and tasty, or heavy and undesirable in flavor. Food chemists also have learned that only within the limits of a very small range in hydrogen ion concentrations is *a maximum of pectin precipitated* and a jelly of desired flavor and fine texture obtained; while outside this range, either no pectin is precipitated or a jelly of poor flavor and texture will result. In the canning of foods it is known that the *length of the sterilization period* is determined in part by the hydrogen ion concentration of the food mass, and that, in general, the higher said concentration the shorter is this fermentation period. It is for this reason that it does not require as long a period for the sterilization of such foods as tomatoes and currants, which are in themselves highly acidic, as for the sterilization of such foods as peas and meats. Some findings concerning the foregoing are reported as follows:

In bread-making, for optimum fermentation period the hydrogen ion concentration should be from cH $10^{-4.5}$ to cH 10^{-5} (pH 4.5–pH 5).

In jelly-making, for maximum yield of pectin and for the most satisfactory texture and flavor of the finished product the jelly mass in the making should be kept within the hydrogen ion concentration range of from cH 10^{-3} to $10^{-3.55}$ (pH 3–3.55).

In canning foods, the cH of tomatoes and some other foods is around 10^{-4} (pH 4), hence the sterilization period is short.

The cH of carrots, beets, and beans is from 10^{-5} to 10^{-6} (pH 5–6), hence the sterilization period must be longer.

The cH of peas, corn, and meat is below 10^{-6}, hence the sterilization period must be still longer.

Bacteriologists have learned that the concentration of hydrogen ions, hence of hydroxyl ions, is a factor in the maintenance of the *life and health of bacteria,* also that different strains of bacteria are active and healthy only in the specific hydrogen ion concentration

environments peculiar to their respective needs. Moderate variations may result in marked modifications of their cultural characteristics, whereas more extreme variations may completely inhibit their growth. Most pathogenic bacteria find their optimum environment at about cH $10^{-7.4}$; which, most significantly, and frequently with disastrous results, is within the normal hydrogen ion concentration range in the blood, lymph, and cells of humans.

Optimum Hydrogen Ion Concentrations as to Bacteria

Streptococci	cH $10^{-7.4}$	pH 7.4
Meningococci	cH $10^{-7.4}$ to $10^{-7.6}$	pH 7.4–7.6
Pneumococci	cH $10^{-7.6}$ to $10^{-7.8}$	pH 7.6–7.8
Diphtheria bacillus	cH $10^{-7.2}$	pH 7.2
Bacillus coli	cH $10^{-7.4}$ for growth	pH 7.4
	cH 10^{-6} for survival	pH 6
	(cH $10^{-4.6}$ cease to multiply)	(pH 4.6)

The physiological chemist has found that the *hydrogen ion concentrations within various digestive masses*, and *within the blood, lymph, and cells* is a factor which determines whether chemical reactions are proceeding normally, the animal being thereby a healthy animal, or whether here and there reactions are not proceeding normally, the animal being thereby a sick one. The following are some reported data in this connection:

Optimum Hydrogen Ion Concentrations as to Humans

Whole saliva	cH $10^{-6.6}-10^{-7.1}$	pH 6.6–7.1
Ptyalin functioning	cH 10^{-6} (Inactive at pH 8, destroyed at pH 3)	pH 6
Pepsin functioning	cH $10^{-1.2}-10^{-3.5}$	pH 1.2–3.5
Sucrase functioning	cH $10^{-6.8}$	pH 6.8
Maltase functioning	cH $10^{-6.8}-10^{-7.2}$	pH 6.8–7.2
Amylopsin functioning	cH $10^{-7}-10^{-7.2}$	pH 7–7.2
Trypsin functioning	cH 10^{-8}	pH 8
Erepsin functioning	cH $10^{-7.7}$	pH 7.7
Steapsin functioning	cH $10^{-7.1}-10^{-7.9}$	pH 7.1–7.9
Blood and lymph	cH $10^{-7.33}-10^{-7.51}$	pH 7.33–7.51

Measurement of hydrogen ion and hydroxyl ion concentrations. The discovery that hydrogen ion and hydroxyl ion concentrations play such a very important part in many phenomena has led to a search for means for measuring the same. Two methods have been developed toward such an end. One of them requires an elaborate apparatus set-up and the measuring depends on the

finding that a solution of definite hydrogen ion concentration exhibits its own electrical potential. The other method is called the *colorimetric* method and depends upon the finding that solutions of definite hydrogen ion concentrations produce definite color and shade effects with selected dyes. As a result, *given a set of solutions of known cH with the known color effects produced with such selected dyes*, it becomes possible, through the agency of these same dyes and by comparison with these known colors, to ascertain the hydrogen ion concentration of any solution which lies within the given known range.

For example. Twelve such dyes which, when applied quantitatively, produce definite color and shade effects within solutions of specific hydrogen ion concentrations, together with the respective cH ranges within which they function, are as follows:

The dye	pH Notations for the cH Range within Which the Dye Functions									
Range finder	3	4	5	6	7	8	9	10		See Figure 85.
Metacresol purple	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	Red to yellow
LaMotte yellow	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	Red to yellow
Brom phenol blue	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	Yellow to blue
Brom cresol green	3.8 — 5.4 Yellow to blue									For these indicators, as with the three foregoing dyes, there are nine different solutions for each dye/pH range, with .2 pH difference (cH $10^{-0.2}$) between successive solutions.
Brom cresol purple	5.2 — 6.4 Yellow to purple									
Brom thymol blue	6.0 — 7.6 Yellow to blue									
Cresol red	7.2 — 8.8 Yellow to red									
Thymol blue	8.0 — 9.6 Yellow to blue									
LaMotte oleo-red B	8.6 — 10.2 Yellow to red									
LaMotte purple	9.6 — 11.2 Purple to red									
LaMotte sulfo-orange	11.0 — 12.6 Yellow to orange									

The dye called *range finder* functions for measuring approximate molar concentrations of hydrogen ions, unless it should happen that the pH of the solution is at *exactly* 3 or 4 or 5, etc. For the measurement of finer differences in hydrogen ion concentrations, a selection from the *other dyes* must be used. The procedure in such measurings is as follows:

First. Set up a series of standard solutions with range finder as dye. 10 cc. each of solutions of pH values 3, 4, 5, 6, 7, 8, 9, and 10 are introduced into eight respective test tubes of like cross section. Five drops of range finder solution, that has been quantitatively prepared for such purpose, are added to each solution. A definite color is obtained with each solution as follows (Fig. 85):

Second. To find the approximate cH of a given solution. Ten cubic centimeters of the solution, whose hydrogen ion concentration it is desired to find,

are put into a test tube of the same cross section as those used for setting up the above standards. Five drops of *range finder* solution are introduced, and the dye and solution are mixed thoroughly. Then, when the color that is obtained within this solution under test with range finder is compared with the colors obtained with this same dye in the above sequence of standard solutions of known cH, it will usually be found to lie between some two of them. Thus

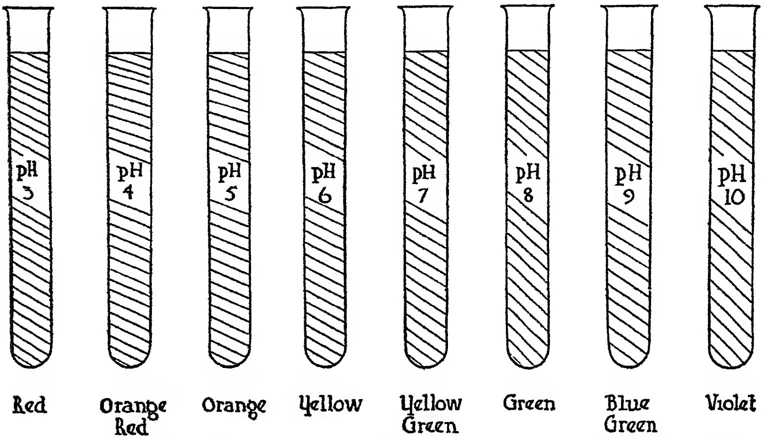


FIG. 85. *Range Finder* as Color Indicator with Solutions of Known Hydrogen Ion Concentrations

can one arrive at the approximate cH of the solution under investigation, since the exact cH will be somewhere between the cH values of the above two adjoining solutions. *For example,* should the color obtained with range finder in the solution under test lie between the colors produced with this indicator in standard solutions of pH 4 and pH 5 (between red-orange and orange), then the exact pH of said solution will lie somewhere within this limited range.

Once the approximate cH of a solution is thus obtained the more exact value can be determined through the use of the indicator dye that functions more accurately for measuring hydrogen concentrations within this limited range. (See table on page 265.) *For example,* should the cH of the solution lie between the above-mentioned pH 4 and pH 5, then brom cresol green is the appropriate indicator to select for further investigation.

Third. Set up the second series of standard solutions that functions with the selected indicator dye. For obtaining more accurately the cH of the given solution, it is next necessary to set up the series of nine standard solutions of known hydrogen ion concentrations within which the cH of this solution lies, together with the specific functioning indicator. These are set up with 10 cc. of each of the nine standard solutions introduced into nine respective test tubes of like cross section with all tubes used for these measurements, and 5 drops of the selected indicator solution are added and thoroughly mixed with each solution. *In the instance of the example* used previously in which the approximate cH of the solution lies between pH 4 and pH 5 and the indicator used for more accurate measurement is found to be ***brom cresol green,*** these nine

standard solutions set up thus should range as to their hydrogen ion concentrations from pH 3.8 to pH 5.4 with 5 drops of this specific indicator added to each (Fig. 86).

Finally. The accurate measurement of the cH of the solution under test. With this second series of standard solutions which contain the functioning measuring indicator set up and ready for use, one is in a position to determine the more accurate cH of the solution under test. This is accomplished by introducing 10 cc. of said solution into a test tube, adding 5 drops of the color

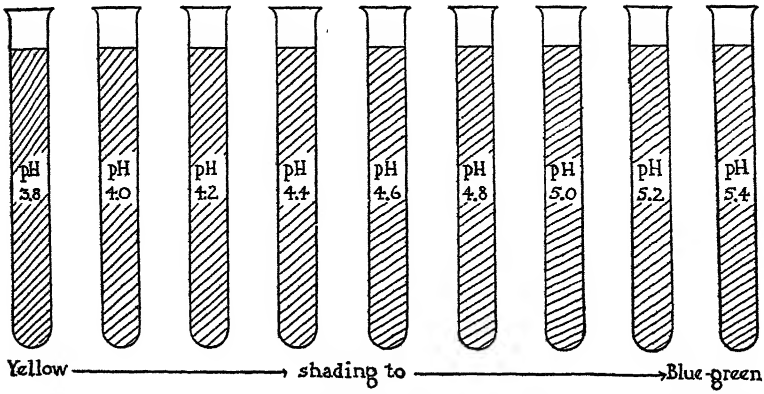


FIG. 86. ***Brom cresol green*** with solutions of pH from 3.8 to 5.4 serves for measuring the hydrogen ion concentration of other solutions within this range.

indicator now in use, mixing well, and comparing the color obtained with the colors in the above series of standard solutions of known cH with this same indicator. The cH of the solution under test will be closest to the known cH of the one of the nine solutions in which the color indicator used gives the closest match. *For example,* should the solution under test with ***brom cresol green*** added find the closest match with this indicator in the standard solution of pH 4.8, then the pH of this solution under test is likewise 4.8, meaning that its cH is $10^{-4.8}$.

The above doubtless seems like a most complicated method for finding the hydrogen ion concentration of a solution. But in a laboratory where such measurements are made frequently, *all* the standard solutions may be kept set up ready for frequent use. With this outlay, only two steps are necessary: *first,* a 10 cc. sample of the solution whose cH one desires to find, with 5 drops of range finder to obtain the approximate cH; *second,* another 10 cc. sample of the solution under test, with 5 drops of the appropriate indicator for finding the more exact hydrogen ion concentration.

Questions

1. When is equilibrium attained as to a weak electrolyte? Example.
2. a. How do concentrations of ionized and un-ionized portions of weak electrolytes at equilibrium differ in respect to each other?
   b. Interpret each of the following expressions:

$$HC_2H_3O_2 \leftrightarrows H^+ + C_2H_3O_2^-$$

$$NH_4OH \leftrightarrows NH_4^+ + OH^-$$

$$HgCl_2 \leftrightarrows Hg^{++} + 2\,Cl^-$$

3. What is the effect upon a lactic acid system previously at equilibrium of:
   a. The evaporation of part of the water?
   b. The introduction of hydrochloric acid?
   c. The removal of some of the lactate ions?

4. The cH of a given solution is .0001. What does this expression mean? What is the cOH of this solution? Why? What does this cOH tell? How many grams of hydrogen ions are present within 1 liter of this solution? How many grams of hydroxyl ions? What electrolyte system other than water must be present? Why?

5. What, in general, is the relationship between the cH and the cOH of a solution when the "reaction" of the solution is: (a) acid, (b) basic, (c) neutral? What is the cH of a neutral solution?

6. The normal cH of whole saliva is about $10^{-6.8}$. What is the cOH of this secretion? Which of these two ions predominates? What is the pH of the saliva? What is the pOH?

7. The best yield of jelly is obtained when the reaction of the jelly mass is about pH 3. What is the cH of the mass? The cOH? How many grams of hydrogen ions would be present in 5 liters of this material? How many grams of hydroxyl ions? What electrolyte system other than water must be present?

8. Certain common molds grow best in a medium of about pH 4. Interpret this expression in terms of both the cH and the cOH of the medium. Is this environment acid or basic? Why?

9. Most pathogenic bacteria grow best in an environment of about pH 7.4. What information is provided by this statement — interpret as fully as you can.

10. Upon what principle does the colorimetric system for measuring the cH of a solution depend?

CHAPTER XIX

Oxidation-Reduction

Oxidation is another word that has come to be used with different meanings in the language of chemistry. In one sense it is used in reference to any reaction of oxygen, the substance, with another substance. We have had, and we shall have, no need to use oxidation in this way. But there are two other and, unfortunately, two different phenomena called oxidation in connection with both of which there is always a complementary phenomenon called reduction. One variety of oxidation-reduction phenomenon plays an essential part in reactions that take place in a number of present-day concerns, as, for example, in the making of metal substances from components of metal ores, in some bleachings and stain removals, in some disinfections, and most importantly, in metabolic processes constantly taking place in cells of plants and animals. The study of such oxidation-reduction processes and contributing phenomena, as well as the bearing they have in the affairs of man, constitutes the chief purpose of this chapter. The second type of oxidation-reduction is interesting, and of great value in a more lengthy study of chemistry, but contributes little of importance to this briefer study and will therefore receive only brief attention.

OXIDATION-REDUCTION FROM ONE VIEWPOINT

Complementary processes. From this viewpoint ***oxidation*** *is the making of a substance with a higher proportion of oxygen than that within the substance from which it originates;* whereas, ***reduction*** *is the making,* at the same time, *of a substance with a lower proportion of oxygen than is present in the parent substance.* Such a complementary process occurs during the reaction between copper oxide and hydrogen to make water and copper:

Copper oxide is reduced to make copper

Hydrogen is oxidized to make water

$$\underset{\text{Oxidizing agent}}{CuO} + \underset{\text{Reducing agent}}{H_2} \longrightarrow H_2O + Cu$$

The *oxidation* part of this reaction is the making of water from hydrogen, the copper oxide which provides the oxygen toward this end being called the *oxidizing agent.* The *reduction* is the

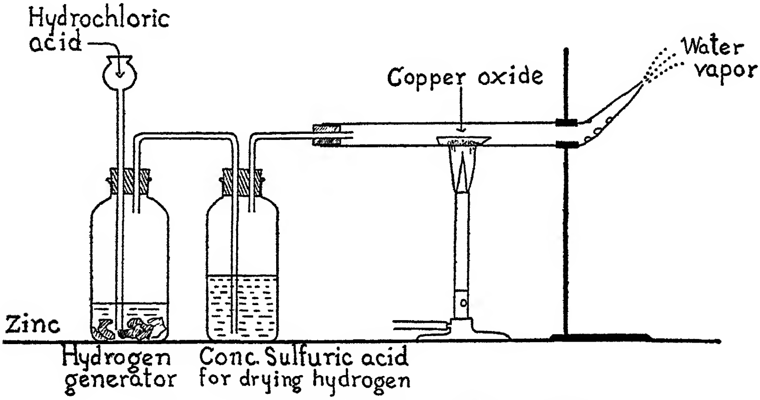


FIG. 87. The Reduction of Copper Oxide by Hydrogen

making of copper from copper oxide; and hydrogen substance which contains the element that is responsible for this reduction, in this case the taking of oxygen away from copper oxide, is called the *reducing agent* (Fig. 87):

By means of an apparatus set up as suggested in the diagram a stream of hydrogen can be passed over copper oxide (present in the boat). As the reaction becomes appreciable only at an elevated temperature, it is necessary to heat the materials in the combustion tube.* As the stream of hot hydrogen passes over the copper oxide a reaction can be observed to take place whereby water is made and escapes from the tube as water vapor, while at the same time, black copper oxide goes out of existence and reddish brown copper substance collects in the boat and on the walls of the combustion tube.* PRECAUTION: Before this heating it is *very important* to make sure that the apparatus is filled with hydrogen, not with a mixture of hydrogen and oxygen. (Why?) To make sure that such is the case a test tube full of the gas escaping from the combustion tube should be collected and tested by burning. (Do not bring the lighted match or burner near the mouth of the combustion tube! Why not?) If the gas thus collected burns *explosively* evidence is thereby provided that a *mixture* of hydrogen and oxygen was collected in the test tube; if it burns quietly, first the top layers in the tube, then successively lower layers, it is evidence that air has all been displaced and that the combustion tube is filled with hydrogen as desired. Heat should *not* be applied to the combustion tube *until assured by more than one successful test* that the combustion tube contains hydrogen rather than a hydrogen-oxygen mixture.

Another oxidation-reduction process becomes involved when lead sulfide reacts with hydrogen peroxide to make lead sulfate and water:

Hydrogen peroxide is reduced to make water

Lead sulfide is oxidized to make lead sulfate

$$\underset{\substack{\text{Oxidizing}\\\text{agent}}}{4\,H_2O_2} + \underset{\substack{\text{Reducing}\\\text{agent}}}{PbS} \longrightarrow PbSO_4 + 4\,H_2O$$

In this reaction the making of lead sulfate from lead sulfide is oxidation, the hydrogen peroxide which gives up part of the oxygen toward such end being the oxidizing agent; the making of water with a lower proportion of oxygen from that within the parent compound, hydrogen peroxide, is reduction, the lead sulfide which pulls oxygen away from this hydrogen peroxide being the reducing agent.

Oxidizing agents. The *oxidizing agents* in the foregoing examples *are oxygen-containing compounds that give up all or part of their oxygen element* to combine with an element or elements provided by the reducing agents concerned. All compounds of oxygen can be regarded as potential oxidizing agents of this sort although they vary greatly as to the ease with which they function in this capacity. Thus, carbon dioxide, water, and silicon dioxide are poor oxidizing agents because they part with oxygen element reluctantly. But hydrogen peroxide, hypochlorous acid, potassium permanganate, potassium chlorate, and oxides of the less active metals, such as silver oxide and copper oxide, are excellent oxidizing agents because of the readiness with which they yield up part or all of their oxygen in the presence of appropriate reducing agents.

Reducing agents. *Reducing agents* for functioning with oxidizing agents *are substances which contain an element or elements with a combining interest in oxygen but which are not satisfied in this respect.* For example: the simple substances hydrogen and carbon are reducing agents because they contain hydrogen element and carbon element which are interested in combining with oxygen to make water and carbon dioxide respectively; the compound carbon monoxide is a reducing agent because its carbon element is only partially satisfied with oxygen. These substances are therefore in a position to reduce appropriately selected oxygen-containing compounds. Other good reducing agents in common use are sulfurous acid which is readily oxidized to make sulfuric acid, oxalic acid which oxidizes to make carbon dioxide and water, and formaldehyde which oxidizes to make formic acid.

Important concerns that involve oxidation-reduction reactions. *Making metal substances from metal oxides.* Only a few metal substances occur already made in nature; most, including the very useful substances iron, zinc, and tin, must be made from compounds of the metal elements present as components of ores found in earth's crust. When such compounds are metal oxides the metal substances can be made by the reduction of said oxides upon the selection of appropriate reducing agents and obtaining right conditions for reactions.

It is after this manner that most of the world's supplies of iron and tin are made, since iron oxides (several) and tin oxides are the chief compounds of these metal elements found in nature. In the making of iron, the iron oxide is mixed with coke (for the sake of the carbon component) and oxygen is admitted; but the furnace is charged with the mixture in such a way that carbon monoxide is first obtained as the desired reducing agent, since it is a better reducing agent than carbon and, being gaseous, is able automatically to make excellent contact with the ore. For some uses of iron, chiefly laboratory uses, a very finely powdered grade is desired that can be better made through the use of hydrogen as the reducing agent. For the making of tin from tin oxide a different sort of furnace is used and carbon of powdered coal is commonly selected as the reducing agent. Equations for some of these reactions are as follows:

(*Hematite*)

$$Fe_2O_3 + 3\ CO \longrightarrow 2\ Fe + 3\ CO_2$$

(*Magnetite*)

$$Fe_3O_4 + 4\ CO \longrightarrow 3\ Fe + 4\ CO_2$$

$$Fe_3O_4 + 4\ H_2 \longrightarrow 3\ Fe + 4\ H_2O$$

(*Stannic oxide*)

$$SnO_2 + C \longrightarrow Sn + CO_2$$

The chief zinc compound thus far found in earth's crust is zinc sulfide. For the making of zinc this compound is first submitted to a reaction treatment whereby zinc oxide is obtained, which, in turn, is reduced through the agency of carbon of powdered coal as in the making of tin:

$$2\ ZnO + C \rightarrow 2\ Zn + CO_2$$

Hydrogen can also be used for reducing tin and zinc oxides; in fact hydrogen can reduce the oxides of all metals beginning with platinum oxides up to (p. 187) and including the iron oxides. And there are other reducing agents that are used on occasion for the

reduction of metal oxides. In all these reactions the metal oxides obviously function as oxidizing agents.

Oxidation-reduction and bleaching. Bleaching takes place when colored substances are destroyed and colorless substances are made. The practical importance of bleaching is a matter of common knowledge. In order to obtain snowy white cotton, linen, and silk our grandmothers removed the brownish pigment — made in plants along with cotton and flax fibers and in silkworms along with silk fibers — by bleaching and they are removed now by bleaching. Stains on white fabrics that are resistant to washing out, such as iron rust stains, ink stains, fruit stains, and those caused by some drugs and disinfectants, are many times removed by bleaching. In the industries, these days, bleaching is resorted to for various purposes. Rags and wood are bleached as part of the process to which they are submitted in the making of white paper; fruits are sometimes bleached and then redyed with desired colors: certainly, neither the red of the maraschino cherries, commonly used for decorative effects in food service, nor the green color of the same cherries used for St. Patrick's day food decoration, is the color that nature made this fruit.

Bleaching by oxidation of pigment. Some colored compounds are attacked by selected substances which function as oxidizing agents, in which event the colored compounds themselves play the part of reducing agents. And, when all products concerned are colorless, bleaching has occurred.

One excellent oxidizing agent for such purposes is hypochlorous acid, which is very eager to yield up its oxygen in order to make the more stable compound hydrochloric acid; at the same time any colored substances which appropriate this oxygen become oxidized:

XYZ	+	HClO	$\longrightarrow$	HCl	+	XYZO
The colored substance		Hypochlorous acid		Hydrochloric acid		Compound or compounds with a higher proportion of oxygen than the colored substance. If colorless, bleaching has occurred.

Hypochlorous acid is used extensively in the industries for the bleaching of cotton, linen, and wood pulp, all of which are associated with yellowish pigments in the plants from which they are obtained. This oxidizing agent can be made in several ways as follows:

Ways for making hypochlorous acid for use in bleaching.

1. Hypochlorous acid is sometimes made from the reaction of chlorine with water. In this case the materials to be bleached are moistened with water and suspended in the atmosphere of chlorine so that the hypochlorous acid will be made in direct contact with the colored substances.

$$Cl_2 + H_2O \longrightarrow HClO + HCl$$

2. Sometimes it is made from hypochlorite salts, such as sodium hypochlorite: (a) in low concentration by hydrolysis of the salt, (b) in higher concentration by reaction with an acid. If the latter method is used, the hypochlorous acid is made in direct contact with the colored substance by dipping the materials first into a solution of the hypochlorite salt and then into the acid solution.

$$\text{(a)}\ NaClO + HOH \longrightarrow HClO + NaOH$$
$$\text{(b)}\ NaClO + HCl \longrightarrow HClO + NaCl$$

3. Another method for making hypochlorous acid is through the use of bleaching powder, sometimes called chloride of lime, which is a complex hypochlorite salt. For such purpose the bleaching powder can be treated with *any* acid, but the acid that frequently functions toward this end is carbonic acid. Thus, bleaching may be produced by dipping the colored material into the solution of bleaching powder and then exposing the moist fabric to contact with carbon dioxide in the air.

$$\underset{\text{(From air)}}{CO_2} + \underset{\text{(On wet fabric)}}{H_2O} \longrightarrow H_2CO_3$$

$$\underset{\text{(Bleaching powder)}}{2\,CaCl(ClO)} + H_2CO_3 \longrightarrow 2\,HClO + CaCO_3 + CaCl_2$$

It is this same hypochlorous acid which whitens clothes during laundering when Javelle water is used, the Javelle water being really a solution of sodium hypochlorite. However, if this bleaching agent is used indiscriminately in laundering, the desired whitening may be unavoidably accompanied by an undesired fading due to a partial bleaching of some colors present in the materials involved. Among the known colored substances that are successfully attacked and bleached by this excellent oxidizing agent are methylene blue and gentian violet, commonly used in the laboratory as bacterial stains, also mercurochrome and acriflavine used as disinfectants. Thus, one possible method for the removal of stains produced by these reagents becomes apparent.

Other good oxidizing agents that are used as bleaching agents are hydrogen peroxide and potassium permanganate. Hydrogen peroxide is used effectively for bleaching the pigments with which nature colors wool, silk, feathers, and hair. Potassium permanganate is an excellent agent to use for removing various stains on white fabrics. Any excess potassium permanganate, which itself is purple, or any brown manganese compound which usually

follows upon the use of potassium permanganate, can be easily removed with a solution of oxalic acid, followed, of course, by thorough rinsing with water.

Bleaching by reduction of pigment. Sulfurous acid has been used for centuries for bleaching certain colored substances. Indeed, it is interesting to learn from the writings of Pliny, a Roman of the first century A.D., that the ancients treated wool with "burning sulfur" to render it white and fluffy. And wool is bleached today after the same method, and so is silk, either in order to secure the desired whiteness, or as a preliminary to recoloring.[1] Certain dried fruits are likewise bleached with this agent, as a means of improving their appearance. One method for securing sulfurous acid as a bleaching agent in direct contact with the colored compound is to first moisten with water the fabrics or fruits carrying the pigment and then suspend them in a closed container or room in an atmosphere of sulfur dioxide made from burning sulfur. The series of reactions concerned is as follows:

$$S + O_2 \rightarrow SO_2 \qquad\qquad SO_2 + H_2O \rightarrow \underset{\text{Sulfurous acid}}{H_2SO_3}$$

Another method for making sulfurous acid for bleaching. A solution of sodium sulfite can be made in one beaker and an exceedingly dilute solution of hydrochloric acid in another beaker. The colored fabrics can then be dipped first into the sodium sulfite solution, then into the acid solution. This alternate treatment can be repeated until any bleaching that is possible has taken place:

$$Na_2SO_3 + 2\,HCl \longrightarrow H_2SO_3 + 2\,NaCl$$

And now comes the question as to the nature of the reaction between sulfurous acid and these colored substances. Since sulfurous acid is a reducing agent, and since the pigments that are associated with the wool and silk fibers, also the pigments that give color to plants and fruits, are probably all oxygen compounds, there is good reason for the belief that the reactions may involve the reduction of the colored substances by the sulfurous acid:[2]

$$H_2SO_3 \quad + \quad \underset{\text{Pigment}}{ABCO} \quad \longrightarrow \quad H_2SO_4 \quad + \quad ABC$$

ABC: Pigment remains, compound or compounds containing a lower proportion of oxygen than in the original pigments.

[1] W. Von Bergen and H. R. Mauersberger, ***American Wool Handbook,*** American Wool Handbook Co., New York, 1938, p. 136.

[2] It is claimed by some that the sulfurous acid enters into direct combination with the colored substances to produce colorless substances instead of functioning in its reducing agent capacity.

Another compound which has long been used for the removal of stains — especially those of iron rust, ink, and fruits — is oxalic acid; and there is good reason to believe that oxalic acid also reacts with the pigments concerned as a reducing agent, the products being carbon dioxide, water, and compounds that result from the reduced pigments:

$$\underset{\text{Oxalic acid}}{H_2C_2O_4} + \underset{\text{Pigment}}{\text{ABCO}} \rightarrow H_2O + 2\,CO_2 + \text{ABC}$$

Incidentally, it should be noted that in most of these common bleaching procedures an acid is present either as the bleaching agent or as another party to the reaction. Consequently the possibility of an accompanying attack of hydrogen ions on the fabric should be anticipated. And the fact is that silk, wool, and rayon fibers are indeed very sensitive to destructive attacks by hydrogen ions; cotton fibers are more resistant, but even these fibers are gradually weakened through such continued contact. In order to minimize this attack, the fabric, after treatment for bleaching, should be rinsed thoroughly, first with a solution of soap, washing soda, ammonium hydroxide, or some other agent capable of providing a low concentration of hydroxide ions, and then with plenty of water.

Some disinfections involve oxidation-reductions of this type. The actual nature of the chemical reactions that result in injury to and death of microörganisms is to a large extent still unknown. However, it is known that among the substances that are effective in the destruction of such organisms are some good oxidizing agents and others that are powerful reducing agents. It is also certain that bacterial cells, as is true of all living cells, contain compounds of carbon, hydrogen, oxygen, and nitrogen which are subject to oxidation, reduction, or both. Therefore, it is reasonable to conclude that when oxidizing agents are responsible for the death of bacteria, it may be because they engage in reactions whereby certain compounds essential to bacterial living are oxidized; on the other hand, when a reducing agent kills bacteria, it may be because said agents become party to reactions whereby certain vital compounds are reduced.

Oxidizing agents as disinfectants. Some of the oxidizing agents that are used in bleaching are also employed as disinfectants. Among them are hypochlorous acid, hydrogen peroxide, and potassiun permanganate.

Chlorine gas is used effectively for disinfecting water supplies and swimming pools; chloride of lime or bleaching powder provides an inexpensive but effective agent for disinfecting feces and urine; Dakin's solution and its various modifications, that came into use

during the first World War as effective wound disinfectants, are essentially solutions of sodium hypochlorite. And in the use of chlorine, or of bleaching powder, or of sodium hypochlorite certainly one of the active disinfecting agents is the oxidizing agent hypochlorous acid, which is made from these substances after the reactions as given under the study of bleaching, and which possibly destroys bacteria by oxidizing certain of their compounds:

$HClO$	+	ABC	$\longrightarrow$	HCl	+	$ABCO$
Hypochlorous acid		Compounds in bacterial cells		Hydrochloric acid		Bacterial remains, compounds containing a higher proportion of oxygen than those of living bacteria.

Another destructive attack on bacteria may be due to a direct reaction of chlorine with proteins of bacterial cells. When hypochlorite salts are used, chlorine is made from the resulting hypochlorous acid after reactions represented thus:

$$2\,HClO \longrightarrow 2\,HCl + O_2 \qquad HClO + HCl \longrightarrow Cl_2 + H_2O$$

Potassium permanganate has been and still is used to some extent as a disinfectant for wound dressings and in irrigations, but the stain left is objectionable and the manganese compound products may be toxic. Hydrogen peroxide is a powerful oxidizing agent, but there is some reason to doubt the practical effectiveness of the three per cent solution of commercial availability.

Reducing agents as disinfectants. Formaldehyde has long been known as one of the most reliable of disinfectants. It is gaseous and therefore automatically penetrating. It is an excellent reducing agent, hence its bactericidal effect is presumed to be due to the reduction of compounds within bacterial cells:

$HCHO$	+	XYO	$\longrightarrow$	$HCOOH$	+	XY
Formaldehyde		Representing compounds in bacterial cells		Formic acid		Bacterial remains, compounds containing a lower proportion of oxygen than those in living bacteria.

In the past, when it was considered necessary to fumigate rooms and their contents following communicable disease, one of the procedures in common use was to burn sulfur candles in a moist atmosphere. Any disinfection that resulted from this practice was probably due to a reduction of compounds within the bacterial cells by the sulfurous acid thus obtained. Although this practice

of fumigation has largely fallen into disuse, the same procedure is still made use of for the preservation of certain fruits, the sulfurous acid made destroying the microörganisms which are involved in decay.

Oxidation-reduction processes are of physiological importance. As has been said previously, many of the vitally important reactions that are constantly going on within animal cells in the process of metabolism include these complementary oxidation-reductions. A consideration of such reactions will form a part of our subsequent study.

A NEWER VIEWPOINT AS TO OXIDATION AND REDUCTION

The foregoing concept of oxidation-reduction as applied to the making of substances with respectively higher or lower proportions of oxygen than in previously existing compounds is useful only when it comes to the study of reactions involving oxygen-containing compounds. But in recent years these terms, oxidation and reduction, have come to be used with quite a different meaning, this time in respect to *charge changes that elements may undergo* as they pass from beginning substances to resulting substances in the course of chemical reactions. In this sense ***oxidation** applies to an increase in the extent of the positive charge* (or to a decrease in the negative charge) *carried by an element;* whereas ***reduction** applies to a decrease in the extent of the positive charge* (or to an increase in the negative charge) *carried by an element* in the course of a chemical reaction. And when, during a reaction, one element undergoes oxidation in this sense another element undergoes a corresponding reduction. This will be made clearer through the following examples.

1. During the reaction of copper oxide with hydrogen, copper

$$\overset{++}{Cu}O + \overset{\circ}{H}_2 \rightarrow \overset{\circ}{Cu} + \overset{+}{H}_2O$$

element is reduced because the charge on its atomic weight is reduced from two units of positive electricity in copper oxide to neutral in copper substance; and at the same time hydrogen element is oxidized because the charge on each of the two atomic weights of this element increases from neutral in hydrogen substance to one unit of positive electricity when combined within water.

2. During the decomposition of potassium chlorate, the element

$$2\,K\overset{+++++}{Cl}\overset{--}{O_3} \rightarrow 2\,K\overset{-}{Cl} + 3\,\overset{\circ}{O}_2$$

chlorine is reduced since the charge on each atomic weight is changed from five units of positive electricity when in potassium chlorate, to one unit of negative electricity when combined within potassium chloride; oxygen is oxidized since the charge on each atomic weight is changed from two units of negative electricity in potassium chlorate, to neutral in oxygen substance.

3. In direct combination of mercury and iodine, the element mer-

$$\overset{\circ}{Hg} + \overset{\circ}{I_2} \rightarrow \overset{++}{Hg}\,\overset{-}{I_2}$$

cury is oxidized, each atomic weight from neutral in mercury substance to two-positive in mercury iodide; iodine is reduced, each atomic weight from neutral in iodine substance to one-negative in mercury iodide.

It will be noted that an oxidation-reduction process from this viewpoint may or may not involve oxygen. Thus, of the three examples given above, it is only during the decomposition of potassium chlorate that oxygen is affected by a charge change, in this instance oxidized; during the other reactions the elements that are mutually oxidized and reduced are elements other than oxygen.

Questions

1. Define oxidation and reduction from the standpoint of the oxygen involvement. Why are reduction and oxidation complementary processes? Illustrate with reference to some specific reduction-oxidation reaction.

2. What is an oxidizing agent? What happens to it during the oxidation-reduction reaction? Name several substances that should be good oxidizing agents.

3. What is a reducing agent? What happens to it during such a reaction? Name several substances that should be efficient reducing agents.

4. In regard to each of the reactions represented by equations on page 272:
   a. What is the oxidizing agent? Why?
   b. What is the reducing agent? Why?
   c. What substance is reduced? Why?
   d. What substance is oxidized? Why?

5. What is the principle involved in the removal of potassium permanganate stains? Suggest at least two possible agents that may function for this purpose. What happens to the compound responsible for the stain during the bleaching? What happens to the bleaching agent?

6. How does hypochlorous acid function in reduction-oxidation reactions? Why must this substance be fresh and made only shortly before use? Assemble equations representative of three different methods in common use for securing hypochlorous acid. What becomes of the pigment in the process of bleaching? What happens to the hypochlorous acid? What precaution should be observed following upon bleaching to prevent a destructive attack on the fabric? Explain. Name several stains that can be bleached by this method.

7. Remembering that many pigments are subject either to oxidation or to reduction, how would you proceed in attempting to remove a stain of uncertain origin?

8. Some pigments are subject neither to oxidation nor to reduction. How do you account for this?

9. From the standpoint of reduction-oxidation reactions, what two attacks are possible upon bacterial compounds? With this in mind account for:

a. The disinfection of water by the use of chlorine.

b. The effectiveness of "Dakin's solution" as a disinfectant for wounds.

c. The functioning of formaldehyde as a disinfectant.

d. The functioning of potassium permanganate as a disinfectant.

10. From the standpoint of charge changes, indicate which of the following reactions include reduction and oxidation. State what elements undergo oxidation and what elements undergo reduction, with reasoning:

a. The reaction of zinc with hydrochloric acid.

b. The decomposition of mercuric oxide.

c. The hydrolysis of copper sulfate.

d. The reaction of oxygen with sulfur dioxide to make sulfur trioxide.

CHAPTER XX

An Introduction to Organic Chemistry

Organic and inorganic compounds. Compounds have been classed as organic and inorganic ever since the earliest days of the science of chemistry, but for many years the differentiation was confused and far from satisfactory. Then in the early 1820's it was pointed out by the great chemist Berzelius[1] that since all so-called organic compounds known at the time were made *only in living cells* of plants and animals they might possess a "vital" or "living force" which it would be impossible for man to duplicate. Thereupon this classification assumed a new and more definite significance, and chemists came to believe firmly in organic compounds as compounds possessed of this inherent vital capacity which rendered it impossible for man to make them in the laboratory; among such compounds were included urea, proteins, carbohydrates, and fats. Contrariwise, all other compounds came to be labeled inorganic, as suggestive of the lack of this vital force; these included certain compounds made in living cells — such as water, carbon dioxide, and hydrochloric acid — but possible also to man's making in beakers and test tubes. The experimental achievement which cast the first shadow of doubt upon this cherished notion as to organic compounds was the making of *urea* in the laboratory in 1828 by a German chemist by the name of Frederick Wöhler.

Wöhler had been heating two inorganic compounds, ammonium sulfate and potassium cyanate, in the hope of obtaining ammonium cyanate, likewise inorganic; but the product which was actually made was *urea!*[1] This was a disturbing discovery, since urea was among the compounds admittedly made in living cells and hitherto supposed possible only as a product of animal metabolism, and now it had been made by mere man! The foundations of a fixed belief were shaken. For, said chemists, "If urea can be made in the laboratory, why not other organic compounds?" And as time went on, other compounds classed as organic were, indeed, made in laboratories, with the result that chemists were forced eventually, with reluctance, to surrender their notion with respect to compounds possessed of "vital force" versus compounds not so possessed. Hence there arose a need for another basis of classification.

[1] F. J. Moore, *A History of Chemistry*, McGraw-Hill Book Co., 1931, p. 135.

In this new classification the original class labels organic and inorganic were retained but with a different significance. *Organic* came to apply only to such compounds as contain *carbon* as one contributing element, while nearly all other compounds, by elimination, came to be labeled *inorganic*. This modern classification basis, then, has only arbitrary significance and it admits inconsistencies in that a *few carbon compounds* which previously had been conceded to be inorganic are still, for convenience, classed as such — among these are carbon dioxide, carbon monoxide, carbon disulfide, carbonic acid, and the carbonates.

Importance of organic compounds. In these modern days, the great importance of organic compounds in the affairs of man is recognized when it is realized that in this group are found many *substances of biological importance*, such as carbohydrates, fats, and proteins; vitamins, enzymes, and hormones; urea and other products of protein metabolism. Organic compounds also include important *drugs* that are used medicinally and compounds used as *disinfectants*. They include as well, thousands and thousands of *materials of commercial importance:* dyes, perfumes, flavors, plastics, rayons, most modern explosives, hydrocarbons of gasoline and like fuel mixtures, and other useful compounds too numerous to mention.

As a matter of fact, so rapidly has the study of this branch of chemistry developed, including the synthesis of new organic compounds, that today, while only about 26,000 compounds of the inorganic variety are known to man, more than 250,000 organic compounds are known, and the list is still growing.

Elements present in organic compounds. For the making of these many and varied substances, nature draws her building materials from a relatively small group of elements. The numerous family of hydrocarbons are built from only hydrogen and carbon. Carbohydrates, fats, alcohols, organic acids, and members of other important groups of organic compounds contain only carbon, hydrogen, and oxygen. Other substances of importance — aniline for instance — are made from carbon, hydrogen, and nitrogen. Proteins are compounds of carbon, hydrogen, oxygen, nitrogen, and usually sulfur and phosphorus. There are also organic compounds that contain chlorine, bromine, or iodine. These nine elements out of the ninety-two building materials are chiefly those upon which nature draws for the making of this great group of compounds, always with *carbon*, it must be remembered, as *one* of the elements.

SOME IMPORTANT FACTS AND THEORIES CONCERNING ORGANIC COMPOUNDS

Organic compounds fall into distinct classes. Some classes of organic compounds are shared with inorganic compounds, for example: there are organic acids, organic bases (called alcohols), and organic salts, and as such these compounds can be expected to undergo reactions after the manner of inorganic acids, bases, and salts. In addition there are some classes peculiar to organic compounds — aldehydes, ketones, carbohydrates, and proteins among them; and compounds within each of these class groups are subject to certain identical chemical behaviors that are characteristic of that class only. Studies of such class reactions will constitute part of our later study.

Speed of reactions involving organic compounds. Reactions as to organic compounds, in contrast with those involving inorganic compounds, are in the main very slow. In many instances they are even inappreciable unless a speeding-up catalyst is present. Consequently, catalysts play a very important part in accomplishing reactions involving organic compounds.

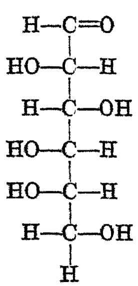
Organic compounds as electrolytes. Organic acids, bases, and salts are mostly weak electrolytes, many of them so weak as to be regarded as nonelectrolytes. This is believed to be one factor which accounts for the slowness of reactions involving these compounds.

Isomers. There are many instances of the occurrence of two or more organic compounds which have the same element make-up and the same empirical composition, hence the same molecular weight. Therefore, although such compounds are different substances since they exhibit different physical and chemical properties, their compositions can be represented by the same empirical formula. An example of this phenomenon, with which the student is doubtless already somewhat familiar, is in respect to the sugars glucose, galactose, and fructose. The formula for the molecular weights of all three of these compounds is $C_6H_{12}O_6$, and yet they are different substances, they have different degrees of solubility and of sweetness; moreover, animal cells use glucose as a reacting partner for oxygen, but possibly not galactose or fructose. *This phenomenon of two or more compounds that have identical empirical composition, so seldom encountered among inorganic compounds, is known as isomerism and the compounds mutually involved are called isomers.* Glucose, fructose, and galactose, accordingly, are isomers of each other. Two other isomeric compounds are ethyl alcohol

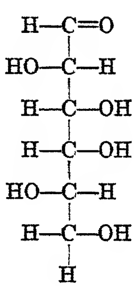
and methyl ether; both have the same composition quantitatively, hence the same molecular weight, as is represented by their common empirical formula C_2H_6O; but they are different substances in that they differ as to some physical properties, and they behave differently in some characteristic chemical ways.

Now these samenesses and differences among isomers are well-known *facts*, the reason for them, however, is *not* known; therefore in order to account for the existence of these isomeric compounds, the chemist, as is his custom, turns to their molecules. Supposedly, says he, while molecules of isomers must have identical composition as far as the varieties and numbers of their atoms are concerned, *the arrangement of the atoms within the molecules of isomers is probably different.* To indicate such difference the chemist resorts to the structural formula which, as the student will recall, is the means used for representing the possible placement of atoms in respect to each other within molecules of substances concerned. For example: molecules of glucose, fructose, and galactose are presumably built from the same number of carbon, hydrogen, and oxygen atoms as represented in the same empirical formula $C_6H_{12}O_6$ for all three, but that they are molecules of different compounds is presumed to be due to different placements of their atoms. This is indicated in their differing structural formulas:

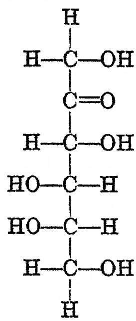
Glucose molecule



Galactose molecule

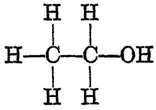


Fructose molecule

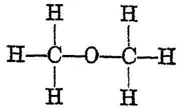


As for the second example, while molecules of both ethyl alcohol and methyl ether are believed to be composed of identical numbers of carbon atoms, hydrogen atoms, and oxygen atoms, as represented in their common empirical formula C_2H_6O, yet they must be molecules of different compounds, hence it is assumed that their atoms are placed differently in respect to each other, and this difference is represented in their structural formulas:

Ethyl alcohol



Methyl ether

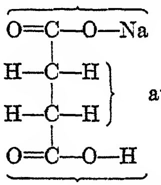


Herein lies one very significant use of structural formulas: to indicate samenesses and differences among isomers.

Many organic compounds are very complex. Among inorganic compounds there are not many, comparatively speaking, that are regarded as complex, but among organic compounds there are many such. This is evidenced as to some organic compounds by their very large molecular weights, but with others, and more significantly, by the complexity of their reactions. For example: a compound which reacts as an acid, a base, and a salt might reasonably be considered complex; or again, if a compound reacts as an acid, a salt, an aldehyde, and a hydrocarbon it might likewise be regarded as complex. This chemical complexity of certain organic compounds often presents difficulties in obtaining desired results in experimental work, in that side reactions due to certain composition features insist upon going on simultaneously with the more specific and desired reaction that one may be attempting to bring into predominance. Many a drug is just such a compound which, because of one aspect of its chemical make-up, is capable of producing some specific physiological attack desired at the time, but cannot be wisely administered because of unfortunate side effects due to other composition features (p. 406).

The "for certain" explanation for such complexity on the part of a compound is not known, but the chemist, as usual, looks to the placement of atoms within its molecule and sees therein as many different atom groups as there are different chemical behaviors as to the compound. For instance, if a compound reacts as an acid, a salt, and a hydrocarbon, it is reasonable to assume that there should be at least three specific atom groups respectively responsible for these reactions. Such a possibility is represented in the following structural formula for the compound concerned:

atom group responsible for *salt* action



atom groups responsible for *hydrocarbon* behavior

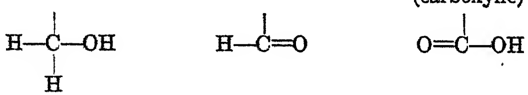
atom group responsible for *acid* reaction

Some compounds are very complex indeed. Hence, it seems reasonable to suppose that the placement of atoms within their molecules must resolve into corresponding complexities; which means, in turn, that structural formulas that have been developed to represent the way things are within such molecules must likewise be complex. The student will meet with some of these representations in later chapters. (See page 408.)

The structural formula. So it is that the organic chemist makes extensive use of structural formulas, whereas the inorganic chemist does not. Two reasons for this have already been presented: namely, (1) to explain the existence of isomers, their samenesses and differences, (2) to explain the chemical behavior of complex compounds. And there are still other uses for the structural formula, among them is the assistance these formulas provide in showing: *first*, wherein compounds within the same class group are alike — for example, wherein all alcohols of the same variety are alike, wherein all aldehydes are alike, wherein organic acids are alike; and *second*, why, therefore, compounds within each class group behave chemically in some respects in identical manner. Such insight is in no way provided by the empirical formulas for these compounds.

Thus, the chemist has come to believe that within molecules of all primary alcohols (p. 306) there must be present an atom group of specific composition. In like manner there is another atom group that must be a constituent of molecules of all aldehydes (p. 316). And there is still another distinctive atom group that must be present within molecules of all organic acids of the one type called carboxylic acids (p. 326). These three different and characteristic atom groups are represented structurally as follows:

Primary alcohol atom group | *Aldehyde atom group* | *Organic acid atom group* (carboxylic)



So it is of great importance that *structural formulas for compounds within each specific class should indicate the presence within their molecules of atom groups identical in structural placement*, thereby explaining why the respective molecules (theoretically), hence the compounds (factually), behave in some identical ways chemically.

It would follow, then, that a structural formula spread out upon a page tells the chemist much at a glance in regard to the compound concerned. Truly a useful sign language!

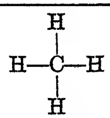
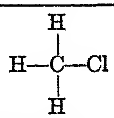
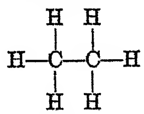
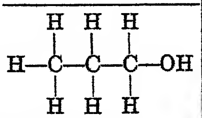
A warning. But with this emphasis as to the structural formula, a warning is in order. It should be continually remembered that this formula is only a *tool,* although an important one, and that it is in reference to something *hypothetical:* the firmly believed-in but nonetheless hypothetical molecule. The practical issue at all times should be the compound itself, its composition and its properties, including its chemical behavior. Moreover, the structural formula must never be mistaken for the formula for the molecular weight of the compound — it should be accepted and used only for what it is intended: namely, such a diagrammatic expression of the way chemists believe atoms to be placed within the molecule of a compound, as provides an imaginary but eminently satisfying explanation for the properties of said compound.

Two basic assumptions. Two assumptions that underlie the whole theory in respect to organic compounds are as follows:

1. The *tetravalency* of the carbon atom, which is in accordance with the fact that the atomic weight of carbon does exhibit a valence of four. The one exception is in respect to carbon monoxide, in which carbon exhibits an unsatisfied valence of two.

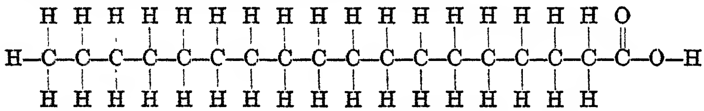
2. The *tendency of carbon atoms to combine with each other* within molecules of compounds.

These beliefs are illustrated in the structural formulas already given, and here are other examples with some observations:

	Empirical formula for molecular weight and molecule	*Structural formula for molecule*	*Observations*
Methane	CH_4		All four valence bonds on the carbon atom are satisfied with hydrogen atoms.
Methyl chloride	CH_3Cl		One valence bond on the carbon atom is satisfied with a chlorine atom, the other three with hydrogen atoms.
Ethane	C_2H_6		The two carbon atoms are "chained" by one each of their valence bonds, the other valence bonds are satisfied by hydrogen atoms.
Propyl hydroxide	C_3H_7OH		The three carbon atoms are "chained" by single bonds, the other valence bonds are satisfied as indicated.

Carbon atoms can be combined through single, double, or triple valence bonds. There is much experimental evidence to support the belief that within molecules of many organic compounds carbon atoms are "chained" (combined) with each other only in ***single bond formation.*** Such is the case within molecules of ethane and propyl hydroxide as is represented in their foregoing structural formulas. In these molecules the two atoms of carbon in ethane molecule and three atoms of carbon in propyl hydroxide molecule are combined in this single bond structure. And within molecules of some organic compounds *many* carbon atoms may be chained thus one to another by single bonds. For example: within the molecule of stearic acid there are presumably eighteen carbon atoms, as is indicated in the empirical formula ($C_{17}H_{35}COOH$) for this compound, and it is believed that the valences of these carbon atoms are in part satisfied through this variety of combination as is represented in the following manner:

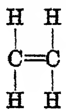
Structural formula for the molecule of stearic acid



Note. The student should observe that valences of the atoms in the above formulas have not been specified as to whether they are positive or negative in nature. The truth is that the theory of positive and negative valence, so useful to the inorganic chemist, does not apply so happily to elements within most organic compounds. Consequently, the organic chemist does not commonly think in terms of the *kind* of valence but usually concerns himself chiefly with the *extent* of valence of elements within compounds.

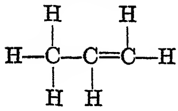
But within molecules of other organic compounds one or more pairs of *carbon atoms are believed to be held in combination with each other, in some instances through two, in other instances through three of their four valence bonds.* Molecules of ethylene (ethene), propene and butene serve as examples of the first variety of compounds, while molecules of acetylene (ethyne), propyne and butyne serve as examples of the second variety of compounds, and their respective structural formulas indicate these conditions as follows:

Ethylene or ***ethene*** C_2H_4

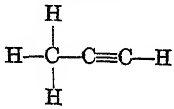


Acetylene or ***ethyne*** C_2H_2

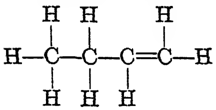
Propene



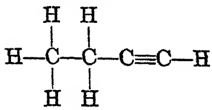
Propyne



Butene C_4H_8

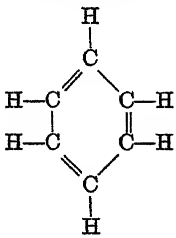


Butyne C_4H_6



Open and closed chain structures. Finally, carbon atoms, presumably, may be combined within the molecule to form either an "open" or a "closed" chain. The examples already cited include only molecules in which carbon atoms appear in the open chain variety of combination. An example of the *closed chain or cyclic* variety is provided by the molecule of benzene as is indicated in the following structural formula. This formula also suggests that the six carbon atoms may be combined through three each of their four respective valence bonds by means of alternate single and double bonds — the fourth valence bond of each carbon atom being satisfied by a hydrogen atom:

Structural formula for Benzene molecule (C_6H_6) *as an example of the closed carbon chain or cyclic variety of combination*



Questions

1. What is the modern basis for the classification of compounds as organic or inorganic? What was the previous basis for such classification?

2. Prepare a list of materials in common use: (a) which you know to be naturally occurring organic compounds, (b) which have come into common use as a result of the development of the science of organic chemistry.

3. Mention several ways in which the development of organic chemistry has affected our modern standard of living.

4. Contrast the speed of reactions involving organic compounds with those commonly encountered among inorganic compounds. How is this difference accounted for? Name one means by which this difficulty is frequently overcome.

5. What are isomers? How is this phenomenon explained?

6. What are two functions of the empirical formula for a compound? The function of the structural formula? Give two reasons why the structural formula has such an important place in the study of organic compounds.

7. State: (a) one basic assumption that *must* be complied with as to structural formulas of all organic compounds; (b) the second basic assumption that may be considered. Looking through the following pages of this text, select structural formulas for at least five compounds and note in each instance how these two basic assumptions are represented.

8. How, theoretically, do organic compounds known as "cyclics" differ from those of the "straight chain" variety? Cite two examples of each, together with their structural formulas.

CHAPTER XXI

Hydrocarbons and Halogen Derivatives

HYDROCARBONS

Important hydrocarbons. The first class of organic compounds to be studied are the *hydrocarbons*. As their name implies, they are substances which are composed of just the two elements carbon and hydrogen, although as individuals they are never called by names that reveal their hydrocarbon nature. Numerous of these compounds are known and some of them, either as individual substances or in mixtures, have important places in everyday concerns.

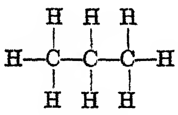
Some ***specific hydrocarbons*** are as follows: *Methane,* made from the decomposition of organic compounds of plant and animal origin, is a component of both "natural gas" and commercially made "illuminating gas." By people in marshy regions it is called "marsh gas" because it bubbles up through water in swamps, having been made from compounds provided by submerged plants. By coal miners it came long ago to be called "fire damp" (fire vapor) in that, made from organic compounds in soft coal and collected in pockets in mines, it was a dreaded fire hazard in the days before mines were electrically lighted when miners went about with lighted candles attached to their caps. *Ethylene*, as well as methane, may be present in "illuminating gas." Within recent years this hydrocarbon has come into prominence as a general anesthetic.[1] It is also being used commercially in recent practice to shorten the period of growth and hasten the ripening of citrus and other fruits. *Acetylene* may also be present in "illuminating gas mixture" and it is the compound which, made in especially devised apparatus, is burned for the illumination of buildings in country places. It is also, it will be recalled (p. 82), one of the fuels burned with commercial supplies of pure oxygen, through the agency of the oxy-acetylene torch, for the purpose of securing the necessary high temperatures — as high as 3500° C. — for the welding and cutting of steel, aluminium, copper, and such other metals as are used in modern construction.

[1] A. B. Luckart and Dean Lewis, "Clinical Experiences with Ethylene-Oxygen Anesthesia." *J. Am. Med. Assoc.*, **81**, 1851–1857 (1923).

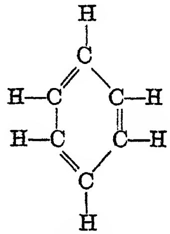
Some well-known *hydrocarbon mixtures* are: benzine [2] used for cleaning purposes; various gasolines, kerosenes, and fuel oils; various so-called mineral oils, used medicinally; and vaselines and paraffins. In nature, many of these hydrocarbons — gaseous, liquid, and solid — are either already present in petroleum oil mixture or are made from other hydrocarbons therein. As a result, petroleum oils constitute an important source of individual hydrocarbons and of hydrocarbon mixtures.

Two major classes. All hydrocarbons fall into two major classes from the standpoint of differing chemical behaviors, hence, differing believed-in structures of their molecules. Without at the moment entering into a presentation of these differences in behaviors, let us consider only the chemist's belief that within molecules of the first class of hydrocarbons the carbon atoms are combined with each other in *open chain* formation; while within molecules of the second class they are combined in *closed chain or ring* formation.

Structural formulas for molecules of hydrocarbons in open and closed chain formation



Propane



Benzene

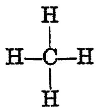
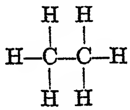
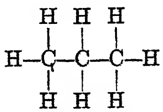
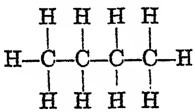
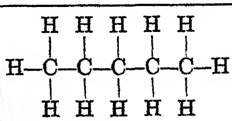
Hydrocarbons of the open chain variety, three classes. We shall give our attention for the present only to hydrocarbons whose molecules are of the open carbon chain variety; of these there are three different series. The commonest hydrocarbons belong to the first and most important series: namely, the *methane series* which is named after the first and simplest hydrocarbon member; but this class of hydrocarbons is also frequently called the *paraffine* series, and more recently, by common international agreement among chemists, the *alkane* series. The other two classes of open chain hydrocarbons have come likewise to be called after their first members: namely, the *ethylene* series and the *acetylene* series of hydrocarbons; and these labels continue to be used although the

[2] The student should be careful to differentiate between *benzine* and *benzene*. Benzine is a mixture of hydrocarbons of the open chain variety. Benzene is a single closed chain hydrocarbon; its formula is given above, also on page 289.

newer nomenclature recommends the labels of *alkene* and *alkyne* for these respective hydrocarbon types.

Methane or paraffine or alkane series of hydrocarbons. The chemist's names for all hydrocarbon members of this series end in *ane,* hence, the advised class label, alk*anes.* The following table specifies by name the first five of the many of these hydrocarbons, also the *known* formulas for their molecular weights, and the related *believed-in* empirical, structural, and semistructural formulas for their molecules.

The ***semistructural formula*** is an abbreviation of the structural formula which is more convenient for representation on the printed page. In this representation the atom groupings are indicated but the valence bonds designated are only those between connecting carbon atoms, or between carbon and other significant atoms.

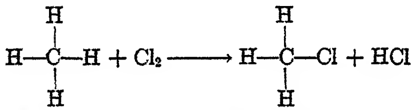
Name of hydrocarbon	*Empirical formula for molecular weight and molecule*	*Structural formula for molecule*	*Semistructural formula for molecule*
Meth*ane*	CH_4		
Eth*ane*	C_2H_6		CH_3—CH_3
Prop*ane*	C_3H_8		CH_3—CH_2—CH_3
But*ane*	C_4H_{10}		CH_3—CH_2—CH_2—CH_3
Pent*ane*	C_5H_{12}		CH_3—CH_2—CH_2—CH_2—CH_3

Can engage only in substitution reactions. Hydrocarbons of this series have come to be called *saturated* compounds, meaning that they cannot combine with any more of any element without first dropping some of their hydrogen. Thus methane and ethane must drop some of their hydrogen before they can combine with chlorine:

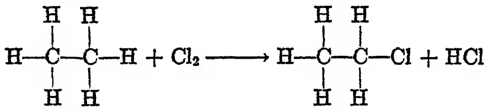
$$\underset{\text{Methane}}{CH_4} + Cl_2 \longrightarrow \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

$$\underset{\text{Ethane}}{C_2H_6} + Cl_2 \longrightarrow \underset{\text{Ethyl chloride}}{C_2H_5Cl} + HCl$$

The theoretical explanation for this fact is indicated in the foregoing structural formulas (p. 293) which suggest that within molecules of these hydrocarbons all four valence bonds of each carbon atom are completely satisfied, either by hydrogen atoms, as in methane, or in part by hydrogen atoms and in part by one or more carbon atoms, hence there are no available valence bonds on said carbon atom for reaching out to "pick up" other atoms. Thus, as to molecules of methane and ethane in reaction with chlorine:

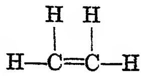
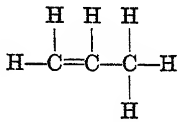
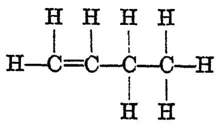
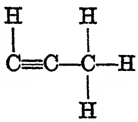
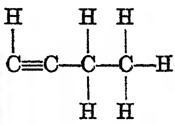


Methane Methyl chloride



Ethane Ethyl chloride

Ethylene or alkene series and acetylene or alkyne series of hydrocarbons. The first three hydrocarbons of the ethylene or alk*ene* series are ethylene or eth*ene*, pro*pene*, and but*ene*. The first members of the acetylene or alk*yne* series are acetylene or eth*yne*, prop*yne*, and but*yne*. The composition of these hydrocarbons is represented in the accompanying table. Explanation for similarities among hydrocarbon members within each of these series is indicated through the structural formulas given. Thus, it is believed that within molecules of all hydrocarbons of the ethylene series at least two carbon atoms are joined with *two* (i.e., double) *valence bonds*, whereas within molecules of all hydrocarbons of the acetylene or alkyne series at least two carbon atoms are believed to be joined by *three* (i.e., triple) *valence bonds:*

Name of hydrocarbon	*Empirical formula for molecular weight and molecule*	*Structural formula for molecule*	*Semistructural formula for molecule*
Ethylene or alkene series			
Ethylene or Eth*ene*	C_2H_4		$CH_2{=}CH_2$
Prop*ene*	C_3H_6		$CH_2{=}CH{-}CH_3$
But*ene*	C_4H_8		$CH_2{=}CH{-}CH_2{-}CH_3$
Acetylene or alkyne series			
Acetylene or Eth*yne*	C_2H_2		$CH{\equiv}CH$
Prop*yne*	C_3H_4		$CH{\equiv}C{-}CH_3$
But*yne*	C_4H_6		$CH{\equiv}C{-}CH_2{-}CH_3$

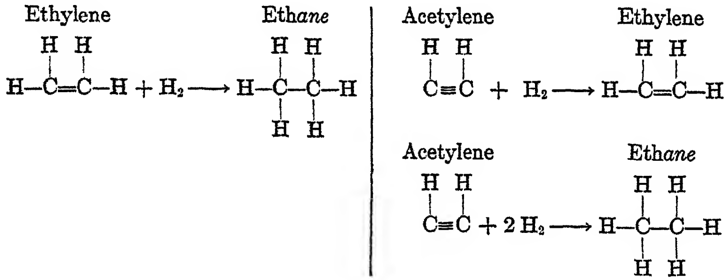
Can engage in direct combination reactions. Quite differently from hydrocarbons of the methane series, hydrocarbons of both of these series are *unsaturated*, that is, they are able to enter into direct combination with more hydrogen, or other selected elements, without dropping any of the hydrogen already present therein. When they do engage in such reaction, the products are either of the saturated or more nearly saturated variety. Such possibilities in respect to ethylene and acetylene are represented as follows:

Ethylene + Hydrogen ⟶ Eth*ane*
$C_2H_4 + H_2 \longrightarrow C_2H_6$
(Unsaturated) (Saturated)

Acetylene + Hydrogen → Ethylene
$C_2H_2 + H_2 \longrightarrow C_2H_4$
(Unsaturated) (More nearly saturated)

Acetylene + Hydrogen ⟶ Eth*ane*
$C_2H_2 + 2\,H_2 \longrightarrow C_2H_6$
(Unsaturated) (Saturated)

The theoretical explanation for this known chemical behavior of these unsaturated hydrocarbons lies in the belief that the double and triple valence bonds between carbon atoms within molecules is not the desirable condition; as a result, where they *do* occur, and given opportunity, the extra one or two bonds "reach out" to "pick up" other atoms with an aim toward establishing a single bond combination between carbon atoms in such locations. And this is what is supposed to happen within the ethylene and acetylene molecules as they engage in reactions with hydrogen and other substances.



Physical properties of hydrocarbons. It is an interesting and significant fact that the *physical states* of hydrocarbons at ordinary temperatures vary to some extent with their molecular weights. Those with low molecular weights, such as methane, ethane, ethylene, and acetylene, are gaseous. With increasing molecular weights there appear, first, hydrocarbons that are volatile liquids including those in benzine, gasolines, and kerosenes; next, hydrocarbons that are still less volatile liquids, such as those in fuel oils; then others with still higher molecular weights that are semisolid and which include those in vaseline; finally, there appear hydrocarbons within the highest range of molecular weights, such as those present in paraffines, and these are solids.

As for *solubilities*, no hydrocarbons are soluble in water but have varying degrees of solubility in alcohol, ether, and carbon tetrachloride; they are very soluble in benzine, gasolines, and the like —

meaning that they are very soluble in each other. These insolubilities and solubilities of hydrocarbons have a practical bearing in various concerns. Herein lies the reason why water is useless in removing stains made on clothing or linen by vaseline or by parafine from the dripping of candles; why alcohol does a little better job in this respect; and why benzine works like magic. Herein, too, lies the reason why in nature hydrocarbons are found in solution in petroleum oils.

Physiological effect. Gaseous and the more volatile liquid hydrocarbons have anesthetic effect. But less volatile members of the group — heavy liquids, semisolid and solid hydrocarbons — are physiologically inert, quite likely because they can neither be inhaled nor penetrate membranes.

Chemical properties of hydrocarbons. ***In reaction with oxygen.*** All hydrocarbons are capable of reacting with oxygen at burning speed. If *adequate oxygen* is provided, the matter products are carbon dioxide and water, as represented in the following equations in respect to methane.

$$\begin{array}{ccccccc} \text{Methane} & + & \text{Oxygen} & \rightarrow & \text{Carbon dioxide} & + & \text{Water} \\ 2\,CH_4 & + & 4\,O_2 & \longrightarrow & 2\,CO_2 & + & 4\,H_2O \end{array}$$

But with *inadequate oxygen* a third product: namely, carbon, is made:

$$\begin{array}{ccccccccc} \text{Methane} & + & \text{Oxygen} & \rightarrow & \text{Water} & + & \text{Carbon dioxide} & + & \text{Carbon} \\ 2\,CH_4 & + & 3\,O_2 & \longrightarrow & 4\,H_2O & + & CO_2 & + & C \end{array}$$

Quantities of oxygen entering reactions with hydrocarbons and of carbon made are in inverse ratios as to each other: the greater the quantity of oxygen entering the reaction the less the carbon made. This is shown in the above equations for reactions with methane, and again in the following equations for reactions of oxygen with ethylene, equal quantities of ethylene being involved in the several reactions:

With adequate oxygen	$2\,C_2H_2 + 5\,O_2 \longrightarrow 2\,H_2O + 4\,CO_2$
With oxygen supply limited	$2\,C_2H_2 + 4\,O_2 \longrightarrow 2\,H_2O + 3\,CO_2 + C$
With oxygen still more limited	$2\,C_2H_2 + 3\,O_2 \longrightarrow 2\,H_2O + 2\,CO_2 + 2\,C$

Of course it is the carbon product which, if present, deposits on beakers in the laboratory and on kettles in the kitchen when burning illuminating gas with inadequate oxygen supplies.

Chemical activity. Comparatively speaking, *saturated hydrocarbons are inactive chemically* whereas *unsaturated hydrocarbons are active.* Methane, ethane, and other saturated hydrocarbons react only slowly, even at high temperatures, with oxidizing agents and the usual acids and bases. But ethylene and acetylene, as

representative of unsaturated hydrocarbons, react with these compounds more or less readily even at ordinary temperatures.

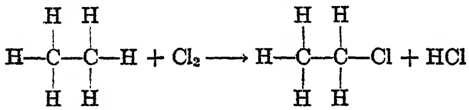
With chlorine and bromine. Of great importance to the chemist is the tendency of all hydrocarbons to react with chlorine and bromine.

Between *saturated hydrocarbons* and chlorine or bromine a *substitution reaction* occurs in which the element chlorine or bromine displaces from part to all of the hydrogen to make substitution products of the specific hydrocarbons and hydrochloric acid or hydrobromic acid. A general statement for such reactions with chlorine, together with equations for reactions with specific hydrocarbons, are as follows; similar statement and examples would follow for reactions with bromine:

Alkane hydrocarbon + Chlorine → Chloroalkane + Hydrochloric acid

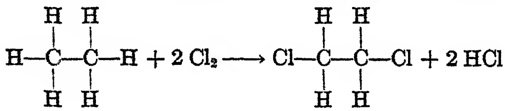
Ethane + Cl₂ → Monochloroethane or Ethyl chloride + HCl

$$C_2H_6 + Cl_2 \longrightarrow C_2H_5{-}Cl + HCl$$



Ethane + Cl₂ → Dichloroethane + 2 HCl

$$C_2H_6 + Cl_2 \longrightarrow C_2H_4Cl_2 + 2\,HCl$$

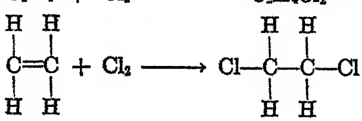


But *unsaturated hydrocarbons react readily in direct combination* with chlorine and bromine. With hydrocarbons of the alkene series, the products of such reactions are known to be chloro and bromo derivatives of alkane or saturated hydrocarbons; which means, theoretically, that the double bond between pairs of carbon atoms in the molecules affected give way to single bonds upon combining with the chlorine or bromine. Thus:

Alkene hydrocarbon + Chlorine → Chloroalkane

Ethylene or Eth*ene* → Dichloroeth*ane*

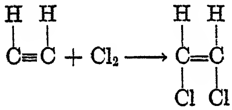
$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$



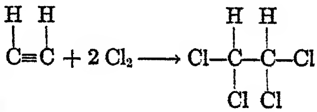
When hydrocarbons of the acetylene or alkyne series engage in such reactions the products are halogen derivatives of either the corresponding alkene or alkane hydrocarbons, depending in part upon the proportion of chlorine or bromine engaging in the reaction. From a theoretical angle, then, this would mean that triple bonds between carbon atoms give way to double valence bonds in the making of alkene derivatives and to single bonds in the making of alkane derivatives. A general statement for reaction with chlorine and examples are as follows; similar statement and similar reactions would, of course, follow from reactions with bromine:

$$\text{Alkyne hydrocarbon} + \text{Chlorine} \rightarrow \begin{array}{c}\text{Chloro alkene}\\ \text{or}\\ \text{Chloro alkane}\end{array}$$

Acetylene or Eth*yne*		Dichloro-eth*ene*
$C_2H_2 + Cl_2$	$\longrightarrow$	$C_2H_2Cl_2$



Acetylene or Eth*yne*		Tetrachloro-eth*ane*
$C_2H_2 + 2\,Cl_2$	$\longrightarrow$	$C_2H_2Cl_4$



It is both impossible and unnecessary in this brief study to elaborate on just why such reactions between hydrocarbons and chlorine and bromine are of great importance to the chemist; suffice it to say that the halogen derivatives of hydrocarbons, and there are many of them, obtained after such reactions or by more devious means, provide parent substances from which many other organic compounds can be made.

Unsaturated hydrocarbons are subject to polymerization. Polymerization is a reaction whereby a compound enters into direct combination with itself to make another compound with a molecular weight that is a multiple of the molecular weight of the original substance. Theoretically, this is accomplished by a direct combination between two or more molecules of the beginning substance to make a correspondingly larger molecule of the resulting substance.

This property applies to unsaturated hydrocarbons, the polymerization of which has become of enormous interest in the concerns of the world in connection with the making of synthetic plastics, including rubber. Two hydrocarbons that are already in use toward this end are ethylene and acetylene. As for the latter, its polymerization results in a compound called vinyl acetylene,

and a catalyst is necessary to accomplish this reaction; one such is a copper salt. Then this compound reacts with hydrogen chloride, after the manner of all unsaturated hydrocarbons, to make chloroprene, which, in turn, polymerizes to neoprene; and neoprene can be substituted for rubber in many of its uses. This series of reactions is represented as follows:

$$\text{Acetylene} \xrightarrow{\text{copper salt}} \text{Vinyl acetylene}$$

$$2\,HC{\equiv}CH \longrightarrow H_2C{=}\underset{\displaystyle H}{\underset{|}{C}}{-}C{\equiv}CH$$

$$\text{Vinyl acetylene} + \text{Hydrogen chloride} \longrightarrow \text{Chloroprene}$$

$$H_2C{=}\underset{\displaystyle H}{C}{-}C{\equiv}CH \quad + \quad HCl \longrightarrow H_2C{=}\underset{\displaystyle H}{\underset{|}{C}}{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}CH_2$$

$$\text{Chloroprene} \xrightarrow{\text{polymerizes}} \text{Neoprene (a rubber substitute)}$$

Rubber. The major component of natural rubber is a hydrocarbon called caoutchouc, formula $(C_5H_8)_n$, which would seem to be an isomer of another hydrocarbon called isoprene, formula C_5H_8. And, upon distillation, caoutchouc actually does yield isoprene and its polymers:

$$\overbrace{C_5H_8 \text{ or } H_2C{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}\underset{\displaystyle H}{\underset{|}{C}}{=}CH_2}^{\textit{Isoprene}} \qquad\qquad \overset{\textit{Caoutchouc}}{(C_5H_8)_n}$$

And this process has at least been partially reversed in that isoprene has been made in the laboratory and polymerized to make synthetic rubber having 800 times the molecular weight of isoprene.

Chemists have long known of the possibility of producing substitutes for natural rubber for many of the uses made of this material; but, until recently, the cost of production has seemed too great to do much about it; also physical properties of the resulting material have not been entirely satisfactory. However, with the inaccessibility of natural rubber supplies and the urgency for even greater quantities of material that will do the same work, and better, for war and industrial needs, for hospital and personal needs, researches in this field are being speeded up enormously. And results seem to be most promising, since chemists now feel assured that materials are being developed with properties that are even better adapted to the various uses made of rubber than is the case as to the natural product itself.

It is known that natural rubber varies greatly as to its properties in unpredictable ways due chiefly to many factors that affect the growth of trees from which it is obtained. But as the result of laboratory researches it now seems probable that, under carefully controlled conditions, synthetic rubber substitutes will eventually be forthcoming that will be especially designed for specific needs and with uniform properties well adapted for meeting said needs.

Already some small articles of equipment, such as catheters in hospital use, are of rubber substitutes; and certainly those who use these articles should

learn how to care for them intelligently. But the promise for the future is considerable, with the prospect of better tires, better rubber fittings of all sorts, better hot water bottles, better rubber heels, etc., etc.

HALOGEN DERIVATIVES OF HYDROCARBONS

Important derivatives. A few halogen derivatives of hydrocarbons are more or less commonly met with. The following are some of these, together with significant items concerning them. *Methyl chloride* derived from methane, and *ethyl chloride* derived from ethane, are both used as local anesthetics. The reason for this use lies in the fact that they are very volatile; consequently, when sprayed on the skin, in changing rapidly from liquid to vapor, they absorb much heat very rapidly from the areas treated, thus chilling and producing numbness in the region affected.

Chloroform or trichloromethane is a general anesthetic for reasons as yet unknown. It has long since been largely replaced by newer and safer anesthetics, but it will always be of interest from an historical viewpoint as one of the first substances used to produce general anesthesia. A virtue of chloroform is that it is not inflammable; but a disadvantage is that it reacts slowly with oxygen in the presence of light and one of the products of this reaction is phosgene, a poisonous gaseous substance.[3] Because of this hazardous tendency chloroform is stored in brown bottles in dark, cool places.

Iodoform or triiodomethane is used as an antiseptic. However, this disinfectant reaction may not really be due to iodoform itself but rather to the substance iodine which is made gradually from iodoform by a reaction the whole story of which is not understood. Iodoform is yellow, solid, and has a somewhat penetrating odor. It is less used now than formerly.

Carbon tetrachloride, sold commercially as "Carbona," is an excellent solvent for fats, gums, and resins. It is used extensively for dry cleaning and is to be preferred for this purpose to gasoline or other hydrocarbon mixtures because it does not burn. It is also used in certain types of fire extinguishers. Medicinally it has proved to be effective in the treatment of hookworm.

Concerning nomenclature. Since the one-valent radicals from methane and ethane are the *methyl* and *ethyl* radicals, monohalogen[4] as well as other monosubstituents on these hydrocarbons are frequently named accordingly as *methyl* and *ethyl chlorides*,

[3]
$$\begin{array}{ccccccc} \text{Chloroform} & + & \text{Oxygen} & \rightarrow & \text{Phosgene} & + & \text{Hydrochloric acid} \\ 2\,CHCl_3 & + & O_2 & \rightarrow & 2\,COCl_2 & + & 2\,HCl \end{array}$$

[4] The halogens are fluorine, chlorine, bromine, and iodine.

bromides, etc. But another method for naming these halogen and other hydrocarbon derivatives involves specifying the particular hydrocarbon concerned, the number (mono, di, tri, etc.) of substituted halogen or other atoms, and, if necessary, specifying by number (1, 2, 3, etc.) the position in the chain of the particular carbon atom on which the substitution has taken place. Finally, such halogen derivatives as have been in use for some time, bear common names. Some of these derivatives and the names applied are given in the table below.

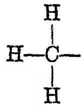
Empirical formula	*Structural formula*	*Name specifying hydrocarbon from which derived*	*Name stressing the two radicals*	*Common name*
Methane derivatives				
CH_3Cl	$\begin{array}{ccc} & \mathrm{H} & \\ & \vert & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{Cl} \\ & \vert & \\ & \mathrm{H} & \end{array}$	Monochloro*methane*	Meth*yl* chloride	
$CHCl_3$	$\begin{array}{ccc} & \mathrm{Cl} & \\ & \vert & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{Cl} \\ & \vert & \\ & \mathrm{Cl} & \end{array}$	Trichloro*methane*		Chloroform
CHI_3	$\begin{array}{ccc} & \mathrm{I} & \\ & \vert & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{I} \\ & \vert & \\ & \mathrm{I} & \end{array}$	Triiodo*methane*		Iodoform
CCl_4	$\begin{array}{ccc} & \mathrm{Cl} & \\ & \vert & \\ \mathrm{Cl}- & \mathrm{C} & -\mathrm{Cl} \\ & \vert & \\ & \mathrm{Cl} & \end{array}$	Tetrachloro*methane*		Carbon tetrachloride or Carbona
Ethane derivatives				
C_2H_5Cl	$\begin{array}{cccc} & \mathrm{H} & \mathrm{H} & \\ & \vert & \vert & \\ \mathrm{H}- & \mathrm{C}- & \mathrm{C} & -\mathrm{Cl} \\ & \vert & \vert & \\ & \mathrm{H} & \mathrm{H} & \end{array}$	Monochloro*ethane*	Eth*yl* chloride	
$C_2H_4Cl_2$	$\begin{array}{cccc} & \mathrm{H} & \mathrm{H} & \\ & \vert & \vert & \\ \mathrm{Cl}- & \mathrm{C}- & \mathrm{C} & -\mathrm{Cl} \\ & \vert & \vert & \\ & \mathrm{H} & \mathrm{H} & \end{array}$	1, 2 dichloro*ethane*		

THE METHYL AND ETHYL RADICALS

Special emphasis should be given to the monovalent *methyl* and *ethyl radicals* because so many compounds contain them as constituents, and their presence is quite likely to contribute important properties to said compounds. Therefore, even when the presence of either of these radicals is not indicated in the name of the compound, the student should be able to recognize its presence through either the empirical or structural representation for the radical within the formula for the compound as a whole. For example: the fact that *acetic acid contains a methyl radical* is not suggested by the name acetic acid, but its presence is indicated by either the semistructural or the structural formula for the acid. Again, the ether that is used to produce anesthesia does not suggest in this name, ether, the presence of the ethyl radical, although the name diethyl ether is more significant. But the formulas — semistructural and structural — for ether do indicate the presence of this radical.

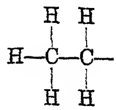
Methyl radical

CH_3—



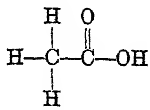
Ethyl radical

C_2H_5—



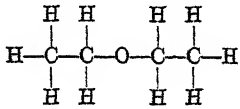
Acetic acid

CH_3—COOH



Diethyl ether

C_2H_5—O—C_2H_5



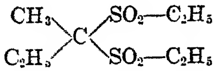
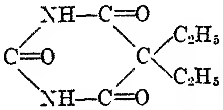
Ethyl radical and drugs. The frequency with which the ethyl radical appears in drugs that have a hypnotic effect has engaged the interest of some chemists who have found it interesting to speculate as to whether this effect may not be due in some degree to the ethyl radical itself. And certainly it is significant that the ethyl atom group is outstanding within molecules of some such typical drugs as shown on the following page.

Many other examples might be cited, as students who become interested in the study of drugs will discover.

Questions

1. What is a hydrocarbon? What is the chief natural source of hydrocarbons? Name at least five compounds that are hydrocarbons. Name at least five hydrocarbon mixtures of common commercial importance.

2. What (factually) is the difference between a saturated and an unsaturated hydrocarbon? How is this difference accounted for theoretically? In

Name of drug	*Formula indicating ethyl atom group*	*Physiological effect of drug*
Ethyl alcohol	$C_2H_5—OH$	A central nervous system depressant, capable of producing stupor
Diethyl ether	$C_2H_5—O—C_2H_5$	General anesthetic
Trional		Hypnotic
Barbital		Hypnotic

general, how do saturated and unsaturated hydrocarbons differ as to chemical activity?

3. With what substance do hydrocarbons make true solutions? Suggest practical procedures for the removal of stains due to vaseline, mineral oil, or the drippings of paraffine candles.

4. The major component of rubber is a hydrocarbon. What should be the result as to the rubber of frequent lubrications with vaseline or mineral oil on equipment made of this material?

5. What three hazards are encountered in using gasoline or other volatile hydrocarbon mixtures as cleaning agents in a closed room? When using hydrocarbon cleaning agents, what precautions should be observed to decrease these hazards?

6. Illuminating gas contains hydrocarbon components such as methane, ethylene, and acetylene:

a. Assemble word and formula equations for the matter and energy transformations which take place when these hydrocarbons burn with adequate oxygen supply.

b. What condition accounts for their occasional burning with a smoky flame? How would you proceed to remedy this condition? Assemble equations (as in a) for the reactions involved under this condition.

c. If same quantities of the same hydrocarbons are burned under conditions specified in a and b, which provides the greater heat product? Reason.

7. What is meant by a halogen derivative of a hydrocarbon? Name several.

8. Why is carbon tetrachloride fire extinguisher preferred for use in automobiles and garages to the type which provides carbon dioxide and water?

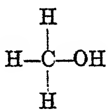
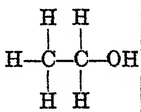
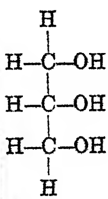
CHAPTER XXII

Alcohols

What is an alcohol? People commonly associate the word *alcohol* only with the two substances methyl or wood alcohol, and ethyl or grain alcohol; actually, however, there are many alcohols. From a composition angle they can be regarded as compounds in which one or more hydroxide radicals have been substituted for part of the hydrogen in hydrocarbons. And, theoretically, as far as the molecule is concerned, it is believed that only one hydroxide atom group can be substituted on each carbon atom. Thus, it is believed that there can be only one alcohol derived from methane, two from ethane.

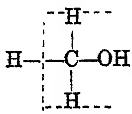
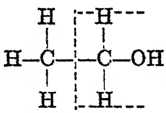
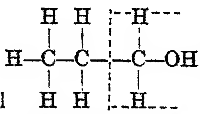
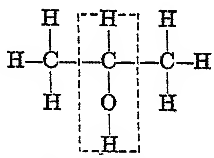
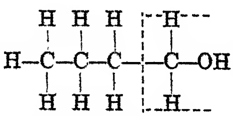
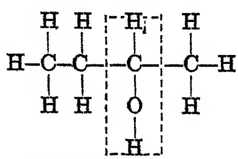
The ***three alcohols of special interest*** in this study are methyl alcohol or methanol, ethyl alcohol or ethanol, and glyceryl alcohol or glycerol; and as we proceed with this study each of these alcohols will be called sometime by one of its names, sometimes by the other.

Various names and formula representations for these alcohols are listed in the accompanying table:

Common name	*Chemist's names*	*Formula for molecular weight and molecule*	*Structural formula for molecule*	*Semi-structural formula for molecule*
Wood alcohol	Methyl hydroxide Methyl alcohol Methanol	CH_3OH		$H—CH_2OH$
Grain alcohol	Ethyl hydroxide Ethyl alcohol Ethanol	C_2H_5OH		$CH_3—CH_2OH$
Glycerine	Glyceryl hydroxide Glyceryl alcohol Glycerol	$C_3H_5(OH)_3$		CH_2OH $CHOH$ CH_2OH

The molecular weights of methyl and ethyl alcohols are known to contain one hydroxide radical weight each, while the molecular weight of glycerol contains three of these radical weights; hence, theoretically, methyl and ethyl alcohol molecules are believed to contain only one hydroxide atom group each, whereas the glycerol molecule contains three of these atom groups. (See formulas in foregoing table.)

Primary and secondary alcohols. As *organic bases*, all alcohols behave chemically in a manner similar to that of inorganic bases, a fact that will be stressed presently. But from the standpoint of reaction with oxidizing agents, alcohols can be sorted out and put into three different classes because of three respectively different responses to such treatment (p. 309). The differentiating class names that have been given to these types of alcohols are *primary*, *secondary*, and *tertiary alcohols*. We shall confine our study solely to the first two varieties of alcohols and for the present shall give

Primary alcohols		*Secondary alcohols*	
Methyl alcohol Methanol	 $H—CH_2OH$	None on methane (why?)	
Ethyl alcohol Ethanol	 $CH_3—CH_2OH$	None on ethane (why?)	
Primary propyl alcohol Primary propanol	 $CH_3—CH_2—CH_2OH$	Secondary propyl alcohol Secondary propanol	 $CH_3—CHOH—CH_3$
Primary butyl alcohol Primary butanol	 $CH_3—CH_2—CH_2—CH_2OH$	Secondary butyl alcohol Secondary butanol	 $CH_3—CH_2—CHOH—CH_3$

attention only to their supposed structural differences. Thus, in the molecule of every *primary alcohol* the hydroxide atom group is believed to be substituted on an end carbon atom in the carbon chain, whereas in the *secondary alcohol* it is believed to be substituted on a carbon atom other than an end one. Examples of the two types of alcohols, with differentiating names and revealing structural formulas for their molecules, are shown in the table on the opposite page.

The student should note from a study of the foregoing structural and semistructural formulas these important items. The primary alcohol atom group always has a distinctive composition ($—CH_2OH$) and its one valence bond reaches out to another carbon atom, save in methyl alcohol molecule as the one exception. The secondary alcohol atom group likewise has its own distinctive composition ($>CHOH$) while its two valence bonds reach out to be satisfied by one of the bonds on each of two other carbon atoms in the hydrocarbon chain. The contrasting compositions of these two alcohol groups, as represented in their respective structural and semistructural formulas, are as follows:

Primary alcohol atom group | *Secondary alcohol atom group*

These items should be thoroughly fixed in mind since they provide a simple and conspicuous means for recognizing whether a compound of given structural or semistructural formula contains a primary or secondary alcohol constituent or both. If so, one is then able to anticipate that said compound should behave like a primary or a secondary alcohol at the point, or points, in its molecule where this group, or these groups, are respectively located. Thus, *primary* propyl alcohol (see foregoing table) will behave like an alcohol, and a *primary* alcohol, at the *one* point in its molecule where this characteristic atom group appears; *secondary* propyl alcohol will behave like an alcohol, and a *secondary* alcohol, at the *one* point in its molecule where this characteristic atom group is located. But the formula for glycerol (see table, p. 305) tells that this compound can be expected to behave like a primary alcohol at *two* points in its molecule, and like a secondary alcohol at *one* point. What some of these chemical behaviors are we shall consider presently.

Physical properties. There are no gaseous alcohols although, as is well known, methyl and ethyl alcohols come close to being gaseous in that they are so volatile. Some alcohols, notably glycerol, are thick, viscous liquids; and many, including carbohydrates (see formulas, pp. 346–347), are solid as to physical state. Volatile alcohols have odors; soluble alcohols are more or less sweet as to taste. Liquid alcohols are solvents for many substances some of which are not soluble in water. This property is taken advantage of extensively in various industries, in pharmacy, and in other important ways, more concerning which will be considered later (pp. 310, 312).

Chemical behavior. ***As organic bases.*** As bases, alcohols can be expected to react accordingly. But their reactions as bases are extremely slow due to their being very weak electrolytes, so weak, indeed, that they are classed among nonelectrolytes. The explanation for this lies, of course, in the belief that when alcohols are in water solution only an ultra-small percentage of their molecules are ionized. Alcohols, therefore, do not yield sufficiently high concentrations of hydroxyl ions to produce an appreciable effect with red litmus. But, despite their ultra-weakness as electrolytes, alcohols do react with acids, as should be expected, to make water and salts; and since the salts from these reactions must always contain hydrocarbons as metal-acting radicals they must be *esters* (p. 340). General statement and examples are as follows:

$$\text{Alcohol} + \text{Acid} \rightarrow \text{Water} + \text{Ester}$$

$$\text{Ethyl alcohol} + \text{Sulfuric acid} \rightarrow \text{Water} + \text{Ethyl sulfate}$$
$$2\,C_2H_5OH + \underset{\text{(dilute)}}{H_2SO_4} \longrightarrow 2\,H_2O + (C_2H_5)_2SO_4$$

$$\text{Methyl alcohol} + \text{Acetic acid} \rightarrow \text{Water} + \text{Methyl acetate}$$
$$CH_3OH + HC_2H_3O_2 \longrightarrow H_2O + CH_3C_2H_3O_2$$

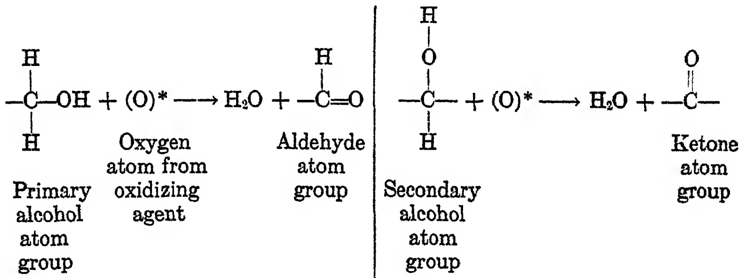
Two difficulties that the chemist must seek to overcome in these reactions between alcohols and acids are as follows. (1) They are, as already mentioned, very slow if unaided. (2) They are decidedly reversible, in that the ester product as it is made has a marked tendency to react with water in a hydrolysis reaction to remake the alcohol and acid. The first difficulty can be overcome by the introduction of an appropriate catalyst and the reaction speeded up accordingly. The second difficulty: namely, the reverse reaction, can be prevented by removal of the water product as fast as it is made through the medium of a dehydrating agent such as concentrated sulfuric acid. In this manner such reactions

can be carried to completion quite satisfactorily in a reasonable length of time.

Alcohols with oxidizing agents. And now for the different responses to attacks of oxidizing agents on primary and on secondary alcohols. The fact is that when a *primary alcohol* reacts with an oxidizing agent the products are *water* and an *aldehyde*. But when a *secondary alcohol* is subjected to such reaction the products are *water* and a *ketone*. Or in brief summary statements:

Primary alcohol + Oxidizing agent → Water + Aldehyde
Secondary alcohol + Oxidizing agent → Water + Ketone

By way of explanation, it is believed that when a primary alcohol is under such treatment, the primary alcohol atom group within the molecule gives place to an aldehyde atom group; whereas in the case of a secondary alcohol under like treatment, the secondary alcohol atom group gives way to a ketone group, a difference made clearer as follows:

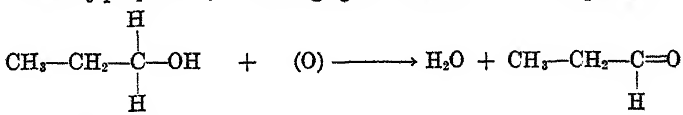


$$—CH_2OH + (O) \longrightarrow H_2O + —CHO \qquad >CHOH + (O) \longrightarrow H_2O + >C{=}O$$

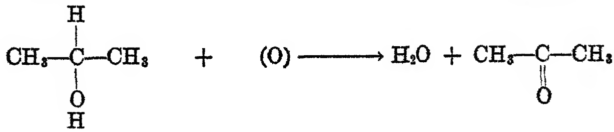
* This expression (O) represents only the oxygen atom provided by the compound that serves as the oxidizing agent, since frequently it is not necessary to complicate the issue by stressing what happens to the rest of the oxidizing agent. But this expression (O) should not be confused with the formula O_2 which is always shorthand in respect to the simple substance oxygen.

Hence in specific application:

Primary propan*ol* + Oxidizing agent → Water + Propan*al*



Secondary propan*ol* + Oxidizing agent → Water + Propan*one* or acet*one*



More attention will be given to these reactions involving primary and secondary alcohols under the study of aldehydes and ketones, and still later in connection with the practical significance of such reactions.

DETAILS CONCERNING METHANOL, ETHANOL, AND GLYCEROL

Methanol or methyl alcohol. These are the preferred names for this alcohol but it can also be called methyl hydroxide, although this name is not usual; and once again, commonly it is called wood alcohol.

Preparation. This alcohol has long been obtained for commercial purposes from the "destructive distillation" [1] of wood, although the chemical reactions concerned in this process are unknown. In recent years, however, a competing method for making methyl alcohol has been discovered which promises a revolution in this industry. After this method methanol is made by direct combination between carbon monoxide with hydrogen in the presence of a favoring catalyst. The formula equation for the reaction concerned is as follows:

$$CO + 2\,H_2 \xrightarrow{\text{catalyst}} CH_3OH$$

Uses. Methyl alcohol has numerous uses. Perhaps the best known is really one of the smallest uses: namely, as a fuel in alcohol burners. The products of burning with *adequate oxygen* are carbon dioxide and water:

$$\begin{array}{ccccccc} \text{Methanol} & + & \text{Oxygen} & \rightarrow & \text{Carbon dioxide} & + & \text{Water} \\ 2\,CH_3OH & + & 3\,O_2 & \longrightarrow & 2\,CO_2 & + & 4\,H_2O \end{array}$$

In much more extensive commercial usage it is employed in leather and textile industries, sometimes because it is a solvent for such materials as shellacs and varnishes, sometimes because it contributes to the making of other useful substances — dyes, drugs, and disinfectants among them. One of these useful reactions is with an appropriately selected oxidizing agent (p. 309) to make formaldehyde or methanal. Methyl alcohol is also used to denature grain alcohol (p. 312).

Physiological effect. When methanol is taken internally it attacks the optic nerve and may thus cause permanent blindness. The same result may follow from continuous exposure to methanol vapor. For this reason methyl alcohol, due to its extensive commer-

[1] Destructive distillation is the process whereby material of plant or animal origin — wood, coal, fuel oils, bones, skin, etc. — are shut up in closed containers out of contact with oxygen and heated to very high temperatures. Numerous substances are made during each of these processes, but by what reactions is not known.

cial uses and consequent exposure of workmen to this hazard, constitutes one of the serious so-called industrial poisons.

Ethanol or ethyl alcohol. These are the two names that are preferred by chemists for this alcohol; but, as has been said previously, by many people it is called grain alcohol. It is the alcohol in most common use and the one present in tinctures and alcoholic beverages.

Preparation. Ethyl alcohol has been known since ancient times and it is made today, as for centuries in the past, by the fermentation of monosaccharids, chiefly glucose, obtained from the hydrolysis of starches or disaccharids. If starch, from barley or any other grain, is the initial carbohydrate employed, the series of reactions involved is as represented below:

$$\begin{array}{ccccc} \text{Starch} & + & \text{Water} & \xrightarrow{\text{diastase}} & \text{Maltose} \\ (C_6H_{10}O_5 \cdot C_6H_{10}O_5)_n & + & n\,H_2O & \longrightarrow & n\,C_{12}H_{22}O_{11} \end{array}$$

$$\begin{array}{ccccc} \text{Maltose} & + & \text{Water} & \xrightarrow{\text{maltase}} & \text{Glucose} \\ C_{12}H_{22}O_{11} & + & H_2O & \longrightarrow & 2\,C_6H_{12}O_6 \end{array}$$

$$\begin{array}{ccccc} \text{Glucose} & \xrightarrow{\text{zymase}} & \text{Carbon dioxide}^{2} & + & \text{Ethyl alcohol} \\ C_6H_{12}O_6 & \longrightarrow & 2\,CO_2 & + & 2\,C_2H_5OH \end{array}$$

Uses. Ethyl alcohol has a much more extensive use as a *fuel*, employed in alcohol burners, than has methyl alcohol and it is a better fuel since, gram for gram, more heat product is made from its burning with oxygen than from the burning of methyl alcohol. This, of course, is due to the fact that more oxygen, hence more transformable chemical energy, is brought into the reaction with grain alcohol than with the same quantity of wood alcohol, a fact which can readily be ascertained through the agency of the following equations for the two reactions concerned:

$$\begin{array}{ccccccc|c} \text{1 gram} & & \text{1.5 grams} & & & & & \\ \text{Methanol} & + & \text{Oxygen} & \rightarrow & \text{Carbon dioxide} & + & \text{Water} & \text{5.33 Calories} \\ 2\,CH_3OH & + & 3\,O_2 & \longrightarrow & 2\,CO_2 & + & 4\,H_2O & \\ & & & & & & & \\ \text{1 gram} & & \text{2.08 grams} & & & & & \\ \text{Ethanol} & + & \text{Oxygen} & \rightarrow & \text{Carbon dioxide} & + & \text{Water} & \text{7.11 Calories} \\ C_2H_5OH & + & 3\,O_2 & \longrightarrow & 2\,CO_2 & + & 3\,H_2O & \end{array}$$

Due to the volatility of grain alcohol, and this applies also to wood alcohol, the kindling temperature of alcohol and oxygen mixture is low and constitutes a fire hazard. For fuel purposes de-

[2] Carbon dioxide made after this manner is collected under pressure in metal tanks to be used in various ways, including therapeutic uses: for inhalations and for making solid carbon dioxide, commonly called "dry ice."

natured alcohol is commonly used, meaning grain alcohol mixed with a small quantity of wood alcohol or some other substance which renders it unfit for use for beverage purposes.

In *hospital* practice, the commonest uses for ethyl alcohol are for alcohol rubs and as an antiseptic. In the *laboratory* it is used as a preservative for biological specimens and as a solvent for materials that are not soluble in water. Its function both as an antiseptic and a preservative depends upon the fact that this alcohol attacks proteins of bacterial cells to destroy them.

Commercially, ethanol has numerous uses. It is the solvent which is employed in various medicinal preparations called tinctures, elixirs, essences, and spirits, as well as in flavor and perfume preparations. Like methanol, it is a solvent for varnishes and shellacs and finds extensive commercial uses in this capacity. Ethyl alcohol is essential to the manufacture of a great many drugs and antiseptics, including ether, chloroform, and avertin (tribromoethane).

Physiological effect. Ethyl alcohol functions as a depressant of the central nervous system to lessen self-control, to produce lack of muscular coördination, and to dull nerve functioning. Consequently, it is classed among drugs that act as central nervous system depressants.

Glycerol. The recommended name for this alcohol is glycerol but if it is desired to stress the presence of the glyceryl radical it can be called glyceryl alcohol; more commonly it is called glycerine. Glycerol is a syrupy liquid, with a sweet taste. It is obtained commercially as a by-product in the manufacture of soap from reaction of sodium hydroxide with fats. The equation involved in such reaction, with glyceryl stearate as the specific fat, is as follows:

$$\begin{array}{ccccccc} \text{Glyceryl stearate} & + & \text{Sodium hydroxide} & \longrightarrow & \textit{Glycerol} & + & \text{Sodium stearate} \\ C_3H_5(C_{17}H_{35}CO_2)_3 & + & 3\,NaOH & \longrightarrow & C_3H_5(OH)_3 & + & 3\,NaC_{17}H_{35}CO_2 \end{array}$$

Uses. Glycerol is another alcohol which has many uses. Among these are its uses: as a sweetening agent, in lotions for chapped hands, and in preparations that are used in the care of a dry mouth accompanying fever. A major use for glycerol in the industries involves its reaction with nitric acid to make glyceryl nitrate, more commonly called nitroglycerine:

$$\begin{array}{ccccccc} \text{Glycerol} & + & \text{Nitric acid} & \rightarrow & \text{Water} & + & \text{Glyceryl nitrate (Nitroglycerine)}^{3} \\ C_3H_5(OH)_3 & + & 3\,HNO_3 & \rightarrow & 3\,H_2O & + & C_3H_5(NO_3)_3 \end{array}$$

[3] From a chemical viewpoint, nitroglycerine is an incorrect name for this compound. It contains the *nitrate* radical ($—NO_3$), not the nitro radical $\left(\rangle NO_2\right)$.

And the nitroglycerine is, in turn, used in the making of many other products—including guncotton, collodion, pyroxylin enamels and lacquers — that have come to be so important in these recent years.

Physiological importance. Glycerol, as previously pointed out (p. 184), is a product of the digestion (hydrolysis) of fats in the intestine. Equations for this reaction with glyceryl stearate are as follows:

$$\underset{\text{(a typical fat)}}{\text{Glyceryl stearate}} + \text{Water} \xrightarrow{\text{steapsin}} \text{Glycerol} + \text{Stearic acid}$$

$$C_3H_5(C_{17}H_{35}CO_2)_3 + 3\,HOH \longrightarrow C_3H_5(OH)_3 + 3\,HC_{17}H_{35}CO_2$$

Also, as will be discussed later, glycerol plays an important part in glucose and fat metabolism in the cells.

Finally, in regard to these three alcohols, let it be remembered that they react chemically as do all alcohols: namely,

1. *As bases* they react *with acids* to make methyl, ethyl, and glyceryl salts or esters (p. 340).

2. With *oxidizing agents* they engage in reactions as follows:

Methyl alcoh*ol*
or methan*ol* $(H—CH_2OH)$ to make water and methan*al* $(H—CHO)$

Ethyl alcoh*ol*
or ethan*ol* $(CH_3—CH_2OH)$ to make water and ethan*al* $(CH_3—CHO)$

Glyceryl alcoh*ol*
or glycer*ol* $\left(\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}\right)$ to make water, aldehydes, and ketones $\left(\begin{array}{lll} CH_2OH & CH_2OH & CHO \\ | & | & | \\ CHOH & C{=}O & C{=}O \\ | & | & | \\ CHO & CHO & CHO \end{array}\right)$

Questions

1. What is an alcohol? What similarities and what points of difference are there between alcohols and inorganic bases?

2. What is the functioning atom group that is characteristic of primary alcohols? Of secondary alcohols? Represent each of these characteristic groups both structurally and semistructurally, indicating their valences.

3. For each of the well-known alcohols — methanol, ethanol, and glycerol:
   a. Give both structural and semistructural formulas.
   b. Give three other names for the compound.
   c. Tell how it is obtained commercially.

4. State reaction expectation for each of the following contacts; illustrate with word and formula equations using glycerol as the alcohol:
   a. An alcohol with an acid.
   b. A primary alcohol with an oxidizing agent.
   c. A secondary alcohol with an oxidizing agent.

5. In what industries is methyl alcohol employed? Why does it constitute an industrial hazard?

6. How is ethyl alcohol made from sucrose (provided, for instance, in molasses or in fruit juices)? Assemble equations for the reactions involved in the process indicating the functioning catalysts.

7. List the various purposes for which ethyl alcohol is used in home or hospital practice. In each instance state the property of this substance which makes it suitable for the use mentioned.

8. Why is it inadvisable to stand a bottle of alcohol or a bottle containing an alcoholic solution, such as a perfume, on a varnished or lacquered surface? Should you accidentally spill the contents of such a bottle on a varnished surface, what would be the best procedure to produce the least damage?

CHAPTER XXIII

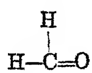
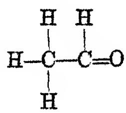
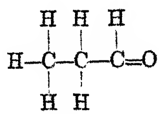
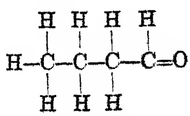
Aldehydes and Ketones

Aldehydes and ketones, unlike alcohols, are peculiarly organic in that they correspond to no compounds of the inorganic variety.

A few of the many aldehydes and ketones are of interest either because of their common or industrial usage, or because of their physiological and pathological bearing. A study of their chemical behavior affords some insight into the chemical behavior of sugars, each of which is, in part, either an aldehyde or a ketone. But even more importantly for our purposes, such study provides a better understanding of the metabolic reactions within animal cells. These two classes of compounds are discussed in the same chapter because of significant similarities and differences, as will be seen.

ALDEHYDES

Representative aldehydes. The only aldehyde that most people have either heard of or know something about is *formaldehyde*, more recently named methan*al*. Others are *acetaldehyde* or ethan*al*, propan*al*, and butan*al*. These are listed below with various formula representations:

Older names	*Chemist's name of more recent date*	*Formula indicating aldehyde nature of compound*	*Structural formula for molecule*
Formaldehyde Formic aldehyde	Methan*al*	H—CHO	
Acetaldehyde Acetic aldehyde	Ethan*al*	CH_3—CHO	
Propionic aldehyde	Propan*al*	C_2H_5—CHO	
Butyric aldehyde	Butan*al*	C_3H_7—CHO	

The aldehyde atom group. The foregoing structural formulas for the several aldehydes concerned indicate the presence within their molecules of identical aldehyde atom groups. The composition of this group and the atom arrangement is believed to be as represented below. This characteristic group has a *valence of one*, hence it can appear in the molecule only at the *end* of the carbon chain. To the presence of this atom group the molecule, hence the compound concerned, is claimed to owe its aldehyde nature.

Aldehyde atom group, structural and semistructural formulas

$$\begin{array}{c} \mathrm{H} \\ | \\ -\mathrm{C}{=}\mathrm{O} \end{array} \qquad\qquad -\mathrm{CHO}$$

Nomenclature. Two methods for naming aldehydes are in use, the older method and the new one. After the older method aldehydes carry names that suggest the corresponding acids: thus *form*aldehyde or formic aldehyde is related to formic acid, while *acet*aldehyde or acetic aldehyde is related to acetic acid. But in more recent years an international committee of chemists has advised that it is preferable to name aldehydes,[1] as are alcohols, in reference to the corresponding hydrocarbons from which they are derived. Hence (see, also, foregoing table):

Formaldehyde is methan*al* (related to methane)
Acetaldehyde is ethan*al* (related to ethane)
Butyric aldehyde is butan*al* (related to butane)

As to our practice, for the first two aldehydes we shall use the older and more familiar names. However, it should be remembered that *al* is the name ending that suggests an *aldehyde* just as *ol* suggests an *alcohol*. The name chlor*al*, therefore, implies that the drug concerned is an aldehyde and it is, in fact, a chlorine derivative of acetic aldehyde with the formula CCl_3—CHO.

Chemical behavior. ***With oxidizing agents and with reducing agents.*** 1. *Factually*, an aldehyde has a marked tendency to combine with more oxygen, taken from another compound, to make the carboxyl part of the corresponding acid. Hence, *theoretically*, the aldehyde atom group must have a tendency to acquire another oxygen atom, taken from the molecule of an oxygen compound, to make the carboxyl atom group in the resulting acid molecule:

[1] The Geneva system of nomenclature, so-called because the international committee meets in Geneva, Switzerland.

$$\underset{}{\text{Aldehyde}} + \underset{\text{(from oxidizing agent)}}{\text{Oxygen}} \longrightarrow \underset{\text{(corresponding to aldehyde)}}{\text{Acid}}$$

$$\underset{\text{(Ethan}\textit{al}\text{)}}{\text{Acetaldehyde}} + \text{Oxidizing agent} \longrightarrow \underset{\text{(Ethan}\textit{oic}\text{ acid)}}{\text{Acetic acid}}$$

$$CH_3-\underset{\underset{O}{\|}}{C}-H \quad + \quad (O) \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-OH$$

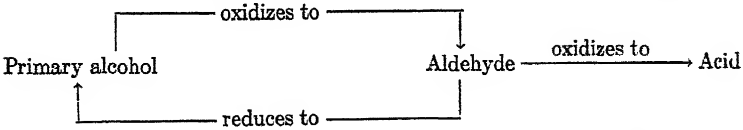
2. Again, *factually*, an aldehyde can be reduced by the addition of hydrogen taken from another substance to make the corresponding primary alcohol. Hence, *theoretically*, the aldehyde atom group, by the addition of hydrogen atoms, becomes reduced to the primary alcohol atom group:

$$\text{Aldehyde} + \underset{\text{(from reducing agent)}}{\text{Hydrogen}} \longrightarrow \underset{\text{(corresponding to aldehyde)}}{\text{Primary alcohol}}$$

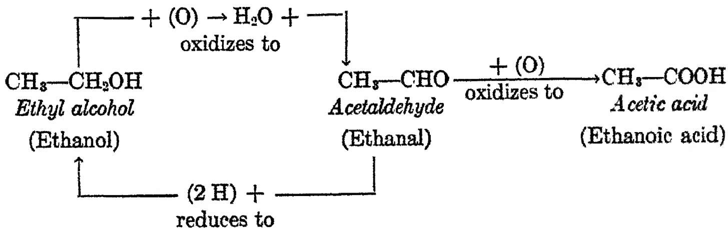
$$\underset{\text{(Ethan}\textit{al}\text{)}}{\text{Acetaldehyde}} + \text{Reducing agent} \longrightarrow \underset{\text{(Ethan}\textit{ol}\text{)}}{\text{Ethyl alcohol}}$$

$$CH_3-\overset{\overset{H}{|}}{C}=O \quad + \quad 2\,H \longrightarrow CH_3-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH$$

Significant observations. *First:* while it is well to have the two foregoing aldehyde reactions stand out as individuals, to be remembered and put to use, it is of equal importance to fit them into the general scheme of reaction sequences among organic compounds. When this is done it appears that an *aldehyde is a transitional compound* between the corresponding primary alcohol and acid in an oxidation series of reactions. Thus briefly summarized:



For example, when acetaldehyde is fitted into this reaction sequence it follows that:



After like manner formaldehyde or methanal is the transitional compound between methyl alcohol and formic acid; and propanal is transitional in the reaction series from propyl alcohol to propionic acid.

It is well to fix these fundamental reaction sequences in mind. It is known that they do occur in beakers and test tubes; and there is evidence that similar oxidation and reduction sequences are of vital concern in metabolic events in the cells. Some of these possibilities will be stressed later, hence this previously obtained information will be very much to the point when that time arrives.

Second: another observation to receive emphasis because of later need, has to do with that portion of the above sequence in which an aldehyde reacts with an oxidizing agent to make an acid:

$$\text{Aldehyde} + \text{Compound of oxygen} \rightarrow \overset{\text{(corresponding)}}{\text{Acid}}$$

Aldehydes are reducing agents. It should be noted that in such reactions the aldehyde acts in the capacity of a reducing agent (p. 271). Like all aldehydes, then, formaldehyde is a reducing agent and its functioning as such provides an explanation for some of its outstanding uses as will be seen presently. Moreover, glucose, galactose, and certain other sugars are "reducing sugars" because they are aldehydes in part (p. 346); and some of the reactions in which they participate, that will receive attention later (p. 355), are due to this fact.

Cupric hydroxide as an oxidizing agent. One of the oxidizing agents frequently employed in laboratory tests for the possible presence of an aldehyde is *cupric hydroxide* [$Cu(OH)_2$]. The reason for this selection is that if reduction occurs it is rendered conspicuous to the eye by the making of vividly *red cuprous oxide* (Cu_2O). It is cupric hydroxide that functions as the oxidizing agent in Fehling's reaction: Fehling's solution I contains cupric sulfate while solution II contains sodium hydroxide. Consequently, when these solutions are mixed, cupric hydroxide, the desired oxidizing agent, is made:

$$CuSO_4 + 2\,NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

Then if a reducing agent is present, such as an *aldehyde*, said cupric hydroxide is reduced to make red cuprous oxide. (See also page 356.) With formaldehyde as the specific reducing agent, the reaction is as follows:

$$\begin{array}{ccccccccc} \text{Cupric hydroxide} & + & \text{Formaldehyde} & \rightarrow & \text{Formic acid} & + & \text{Cuprous oxide} & + & \text{Water} \\ 2\,Cu(OH)_2 & + & H\text{—}CHO & \longrightarrow & H\text{—}COOH & + & Cu_2O & + & 2\,H_2O \end{array}$$

Subject to polymerization. A third chemical property of aldehydes lies in their marked tendency to polymerize. *Factually,* this means that a number of molecular weights of an aldehyde enter

into *direct combination with each other* to make a compound of n times the molecular weight of the original aldehyde. *Theoretically* explained, this would mean that n molecules of the aldehyde combine to make a polymer molecule of n times the weight of the parent aldehyde molecule. For example:

$$\text{3 molecules of formaldehyde} \left\{\begin{matrix}\text{combine} \\ \text{to make}\end{matrix}\right\} \text{1 molecule of paraformaldehyde or paraform}$$

$$3\ H{-}CHO \longrightarrow (H{-}CHO)_3$$

$$\text{3 molecules of acetaldehyde} \left\{\begin{matrix}\text{combine} \\ \text{to make}\end{matrix}\right\} \text{1 molecule of paracetaldehyde or paraldehyde}$$

$$3\ CH_3{-}CHO \longrightarrow (CH_3{-}CHO)_3$$

Paraform and paraldehyde, as they are commonly called, are, therefore, *polymers* of formaldehyde and acetaldehyde respectively. *Paraldehyde* is used medicinally as a hypnotic. *Paraform* is a solid powdery substance; it is present in "formaldehyde lamps," so called because when the paraform is heated it decomposes readily to make gaseous formaldehyde; hence paraform becomes a handy source of this disinfectant:

$$\underset{\textit{Paraform}}{(HCHO)_3} \longrightarrow \underset{\textit{Formaldehyde}}{3\ H{-}CHO}$$

But it is a significant fact that, despite the manner of their making, polymers of aldehydes do not behave chemically as aldehydes.

Formaldehyde or methanal. Formaldehyde is a gaseous substance with a penetrating odor and when inhaled it is very irritating to the mucous membrane of the nasal passages. It is very soluble in water, a property which is taken advantage of commercially by collecting it in water for convenient sale distribution. Thus, it is a 35 to 40 per cent solution of formaldehyde which is sold under the familiar name of *formalin*. Commercially, formaldehyde or methanal is the most important of the aldehydes. It has limited uses in hospitals and laboratories but numerous uses in industries.

In *hospital practice*, formaldehyde is used as a *disinfectant* and is still regarded as one of the most reliable of gaseous bactericides. For this purpose formaldehyde is commonly used in 2 to 4 per cent solution. The manner of its reaction as a disinfectant is not certain, but knowing that it is an aldehyde, hence a reducing agent, it is a good reasoning guess — but a *guess only* — that it may

reduce the proteins in the bacterial cells after a reaction represented thus (see also page 277):

$$\underset{\text{H—CHO}}{\text{Formaldehyde}} + \underset{\text{(Oxygen compounds)}}{\text{Bacterial proteins}} \longrightarrow \underset{\text{H—COOH}}{\text{Formic acid}} + \underset{\text{bacterial remains}}{\text{Compounds of}}$$

The use of this aldehyde for such purpose is suitable for two reasons: first, because of its effectiveness as a bactericide; second, because, from a hospital housekeeping angle, it can be used without injury on all such surfaces as can be treated harmlessly with water. One disadvantage that accompanies the use of this disinfectant is that solutions of formaldehyde are more or less irritating to the skin, an effect which is perhaps due to a reaction with proteins of the skin tissue cells. For this reason, in using formaldehyde, the skin should not be exposed to contact with it unnecessarily, nor should more concentrated solutions be used when a dilute solution would be effective.

A *medicinal usage* of formaldehyde is as a *urinary antiseptic*, that is, to inhibit the growth of any bacteria that may have invaded the urinary tract. It is made in this region from the drug hexamethylenamine, or methenamine, after rather a neat method. This drug is inactive in alkaline environment but *active in acid environment.* Hence, when absorbed into the blood it remains unchanged in the alkaline blood, but when excreted into the acid urine in the urinary tract it reacts with water to make the desired *formaldehyde* in exactly the place where it is needed and where, presumably, it attacks bacterial compounds in the same manner as elsewhere. The equation for the reaction is as follows:

$$\text{Hexamethylenamine} + \text{Water} \rightarrow \text{Formaldehyde} + \text{Ammonia}$$
$$(CH_2)_6\text{—}N_4 \quad + \quad 6\,H_2O \rightarrow 6\,H\text{—}CHO \quad + \quad 4\,NH_3$$

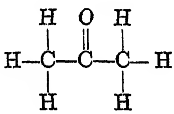
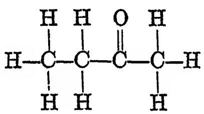
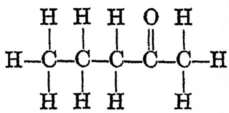
In the *laboratory* formaldehyde is employed as a preservative for biological and pathological specimens, and as a "fixative" for material on bacterial slides. In both of these uses, aside from the attack on bacteria, the aldehyde reacts with the proteins present in some unexplained manner to make insoluble compounds which results in the "stiffening" of specimens and the "fixing" of material on microscopic slides.

Industrially, as an exceedingly reactive and not expensive compound, formaldehyde is used in numerous ways. Among such are its various uses in leather, textile, and dye industries, and in the making of synthetic plastics such as Bakelite. To follow the reasons for these uses of formaldehyde would be difficult or impossible and is outside the province of this study.

KETONES

Representative ketones and their naming. The ketone of most frequent mention is *acetone.* It is the most important ketone commercially, and it is the one of pathological concern which appears in the urine when there is faulty fat metabolism in the cells.

Nomenclature. From a chemical angle the name *acetone* is a misnomer in that this ketone is not related to either acetaldehyde or acetic acid; a more logical name is *propanone* since acetone is really a propane derivative. The name acetone, however, has such a fixed hold in industrial practice that it will probably predominate indefinitely. But the student should know that acetone is really propanone, the name ending *one* quite significantly applying to ketones. (See accompanying table.)

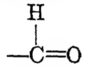
Common name	*Name suggesting related hydrocarbon*	*Structural formula for molecule*	*Semistructural formula for molecule*
Acetone	Propan*one*		$CH_3—CO—CH_3$
	Butan*one*		$CH_3—CH_2—CO—CH_3$
	2-Pentan*one*		$CH_3—CH_2—CH_2—CO—CH_3$

Acetone or propanone is the first ketone derivative that is possible from the hydrocarbons of the methane series, none being obtainable from either methane or ethane. The next ketones in sequence are, therefore, butanone, pentanone, etc. These three ketones are listed with their formula representations in the above table.

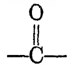
Characteristic atom group and valence. Theoretically, the atom group which is believed to be present within molecules of all ketones has a composition and valence as represented as follows:

Quite appropriately the ketone atom group is represented in contrast with that of the aldehyde:

Aldehyde



Ketone



Again, it should be observed that the ketone group with its *valence of two* cannot appear at the end of the carbon chain, whereas, as previously mentioned, the aldehyde group with its valence of one does appear at the end of said chain. These relationships should be clarified through a study of the contrasting formulas for ketones (p. 321) with formulas for aldehydes (p. 315).

Chemical behavior with oxidizing agents. Like aldehydes, ketones are transitional compounds between alcohols and acids in an oxidation series of reactions. But there are these important differences. It is *known* that:

1. Ketones arise from the oxidation of the corresponding secondary alcohols. (How is it with aldehydes?)

2. A ketone oxidizes to make an acid (or acids) containing less carbon than the ketone concerned. (Again, how is it with aldehydes?)

A secondary alcohol $\xrightarrow{\text{oxidizes to}}$ a ketone (corresponding) $\xrightarrow{\text{oxidizes to}}$ an acid containing less carbon.

3. Oxidations involving ketones do not take place as readily as do those involving aldehydes, hence only excellent oxidizing agents can be used with appreciable results.

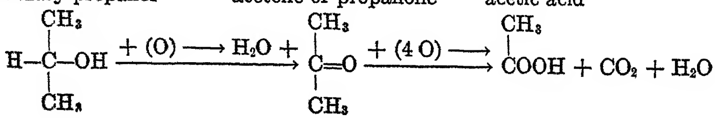
By way of a *theoretical* explanation for the appearance of an acid product with less carbon content, it is claimed that when a ketone molecule is oxidized its chain of carbon atoms is broken at the point where the ketone atom group is located instead of remaining intact as when the aldehyde molecule is oxidized. To apply this oxidation sequence to that involving acetone or propanone the following are represented happenings:

Factually

Secondary propanol $\xrightarrow{\text{oxidizes to}}$ Acetone or propanone $\xrightarrow{\text{oxidizes to}}$ Acetic acid + Carbon dioxide + Water

Theoretically

1 molecule of secondary propanol — 1 molecule of acetone or propanone — 1 molecule of acetic acid



This series of reactions involving ketones as intermediate compounds, as in the case of the aldehyde sequence, is fundamental and should be fixed thoroughly in mind for application as need arises.

When a *ketone is reduced by the addition of hydrogen* the product is the secondary alcohol. But, while important among organic reactions, in this study the chief concern as to the chemical behavior of ketones is with the oxidation sequence stressed.

Acetone. Once again, the ketone of chief commercial usage is acetone. This ketone is a very volatile liquid with a sweetish odor and it is an *excellent solvent* for many materials, including fats and varnishes. In this last-mentioned property lies the reason for its use in the cleansing of garments, in paint removers, and as a solvent for "liquid nail polishes." In its capacity as solvent, as is also true of methyl and ethyl alcohols and of formaldehyde, acetone has contributed very largely to the advancement of the making of rayons, artificial leathers, plastics, and many other materials of modern usage.

Because of its chemical activity acetone is used in the manufacture of many compounds, including some drugs.

ALDEHYDES AND KETONES OF PHYSIOLOGICAL IMPORTANCE

Normally. Three such compounds that are of normal significance physiologically are acetaldehyde, pyruvic aldehyde, and pyruvic acid. Formulas for these compounds are as follows:

Acetaldehyde

$$\begin{array}{l} CH_2 \\ | \\ CHO \end{array}$$

Pyruvic aldehyde

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CHO \end{array}$$

Pyruvic acid

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ COOH \end{array}$$

These substances are believed to appear in the cells as intermediate metabolic compounds: acetaldehyde in the oxidation of glucose, fats, and proteins; pyruvic aldehyde and pyruvic acid in the oxidation of glycerol and glucose (pp. 466, 472, 484).

Pathologically. Acetone and diacetic acid (frequently called acetoacetic acid) are known to be of considerable pathological importance. Formulas for their molecules are as follows:

Acetone

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array}$$

Diacetic acid
or Acetoacetic acid

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_2 \\ | \\ COOH \end{array}$$

When there is a failure in normal metabolism of fats, as in severe diabetes or in starvation, these ketones are excreted, appearing in large quantities in the urine and in smaller quantities in perspiration. At such times acetone, because of its peculiar sweetish odor, can be detected in the breath of the patient. These two substances are spoken of as "ketone bodies" and their presence in the urine is called "ketonuria" (p. 472).

More will be said concerning the occurrence and significance of these five aldehydes and ketones when metabolic reactions are presented in greater detail (Chapter XXX). But it is advisable for the student to become familiar with these substances at this time.

SUGARS ARE ALDEHYDES OR KETONES

Notable among common sugars which are either aldehydes or ketones are the following (see pp. 346–348):

Aldehydes	*Ketone*	*Neither*
Glucose	Fructose	Sucrose
Galactose		
Maltose		
Lactose		

Semistructural formulas for molecules of glucose and fructose which indicate the presence and location of their respective aldehyde or ketone atom groups are as follows:

Glucose

$$\begin{array}{l} CHO \longleftarrow \text{Point at which glucose molecule acts like an } \textit{aldehyde} \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Fructose

$$\begin{array}{l} CH_2OH \\ | \\ CO \longleftarrow \text{Point at which fructose molecule acts like a } \textit{ketone} \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

It follows, therefore, that the four *aldehyde sugars* mentioned are all subject to oxidation, at the point at which they are aldehydes, to make the corresponding acids (p. 357). As for *the ketone sugar*, fructose, it reacts with oxidizing agents after the manner of all ketones to make acids of lower carbon content, hence with a break in the chain of carbon atoms within its molecule (p. 355).

It is in respect to such reactions that these five sugars, and others not mentioned in this text, function as reducing agents, hence the source of the label "reducing sugars."

Questions

1. Represent the composition of the aldehyde atom group both structurally and semistructurally.

2. Aldehydes are referred to as transitional compounds between alcohols (of what variety?) and acids. Illustrate this in relation to methanal.

3. What is the product of the oxidation of butanal? What is the product of the reduction of butanal? Represent the reactions involved by equations.

4. What is the principle underlying Fehling's reaction? Why, presumably, is glucose subject to this reaction? Name at least three other compounds which will react in a similar manner.

5. On the basis of its being an aldehyde, account for the disinfectant function of formaldehyde. What kind of an attack is made on bacterial compounds? Account for the irritating effect that formaldehyde has on the skin.

6. Make a tabulation of the various ketones of importance mentioned in this chapter, noting: (a) names; (b) structural and semistructural formulas, indicating the characteristic atom group; (c) uses or other items of significance.

7. Make general statements as to the product that results from: (a) the reduction of a ketone; (b) the oxidation of a ketone.

8. Acetone is commonly used to remove "liquid nail polish." How does it function in this capacity? Why do the nails frequently become dry and brittle when subjected to this treatment?

CHAPTER XXIV

Organic Acids. Organic Salts. Esters

ORGANIC ACIDS

The study of organic acids should meet with at least a beginning on familiar ground. *First:* the acids of food importance that everyone has some personal acquaintance with are of the organic variety. Conspicuous among these are the acids which are components of common fruits such as tartaric acid in grapes and citric acid in lemons; the acid component of vinegar or acetic acid; and the acid of sour milk or lactic acid. *Second:* from a chemical viewpoint, organic acids are, indeed, acids, consequently certain of their chemical characteristics can already be anticipated.

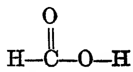
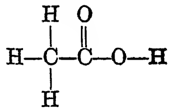
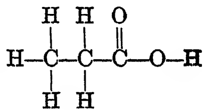
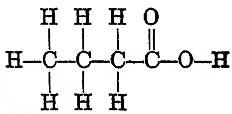
Carboxyl atom group, composition and valence. But before going further it is important to learn that the inorganic chemist and the organic chemist use formulas for these acids that look quite differently. The former, after the manner of our previous study, stresses the two radical parts: namely, the replaceable hydrogen radical and the acid radical. But the organic chemist is interested in indicating that, according to belief, within molecules of organic acids of the type of our present study, the replaceable hydrogen atoms which are responsible for the acid nature of the compounds must always appear within atom groups of identical composition and structure. This characteristic atom group is called the carboxyl, and, since it is built around the *end* carbon atom of the open hydrocarbon chain, the carboxyl, as a whole, must have a valence of one; its structural and semistructural formulas are as follows:

The carboxyl group

$$\begin{array}{c} O \\ \| \\ -C-O-H \end{array} \qquad\qquad -COOH$$

The presence of the carboxyl in specific acids is indicated in their formulas as given in the following table; **H,** in heavier type, is intended to indicate the replaceable hydrogen atom, hence

the hydrogen that is responsible for the acid nature of the compound.

Older name and new name	*Formula after inorganic method*	*Structural formula*	*Semistructural formula*
Formic acid Methan*oic* acid	$HCHO_2$		$H{-}COOH$
Acetic acid Ethan*oic* acid	$HC_2H_3O_2$		$CH_3{-}COOH$
Propionic acid Propan*oic* acid	$HC_3H_5O_2$		$CH_3{-}CH_2{-}COOH$
Butyric acid Butan*oic* acid	$HC_4H_7O_2$		$CH_3{-}CH_2{-}CH_2{-}COOH$

In general, then, the number of carboxyl atom groups in the molecule of the acid is determined by the number of replaceable hydrogen atoms present therein, and vice versa. Thus:

Formic acid molecule has *one* carboxyl group,
since it has *one* replaceable hydrogen atom.

Acetic acid molecule has *one* carboxyl group,
since it has *one* replaceable hydrogen atom.

Tartaric acid molecule has *two* carboxyl groups (p. 329),
since it has *two* replaceable hydrogen atoms.

Citric acid molecule has *three* carboxyl groups (p. 330),
since it has *three* replaceable hydrogen atoms.

Therefore, it follows that if the student is provided with the formula for an acid, structural or semistructural, it should be possible to anticipate which, and how many, hydrogen atoms are replaceable by metal atoms. More of this subject presently, but this insight into the way things are presumed to be within organic acid molecules is all to the good and worth beginning to notice.

Nomenclature. As should be anticipated, the better known acids, such as formic and acetic acids, have handed-down names which have become so fixed that they will doubtless persist. But according to more recent recommendations (footnote, p. 316) monocarboxylic acids have received names which, like those for alcohols, aldehydes, and ketones, suggest the hydrocarbons from which they are derived with *oic* as ending. Examples are given in the foregoing table.

Familiar and important organic acids. Many organic acids, associated with their salts, occur in fruits. And one important group, the so-called fatty acids, are made from the hydrolysis of fats. The following table lists some of the more common organic acids and a few which, although less familiar, are important physiologically. It also cites items of interest concerning them.

Chemical behavior of acids. As is true of all acids the following are some of the reactions to be expected from organic acids:

As electrolytes. They dissociate in water solution to yield hydrogen ions and acid radical ions. Thus, for such portions as ionize, reactions take place on the part of tartaric and acetic acids as represented below:

$$H_2C_4H_4O_6 \longrightarrow 2\,H^+ + C_4H_4O_6^{--}$$
$$HC_2H_3O_2 \longrightarrow H^+ + C_2H_3O_2^-$$

Almost all *organic acids are weak,* that is, when in water solution less than 50 per cent portions of said acids are ionized. Oxalic acid is at the turning point between weak and strong, its strength being nearly that of sulfuric acid (p. 238). It follows, therefore, that oxalic acid is capable of yielding a sufficiently high concentration of hydrogen ions to render it a dangerous substance to have around where a careless person might possibly mistake it for a prescribed medicine. Such tragic mistakes have happened. All other organic acids of common occurrence, including acetic and lactic acids, the acids of fruits, and fatty acids, are weak enough to be relatively harmless.

From a chemical activity viewpoint, since activity varies with the strength of the acid as an electrolyte, it follows that the activity of almost all organic acids, *as acids,* is on the downward scale from active (p. 238). Thus, oxalic acid is fairly active, tartaric acid is less active, citric and lactic acids still less so, while acetic acid is a decidedly weak acid — the least active of those mentioned. These differing activities, commensurate with their strengths as acids, determines the speed with which they engage in reactions.

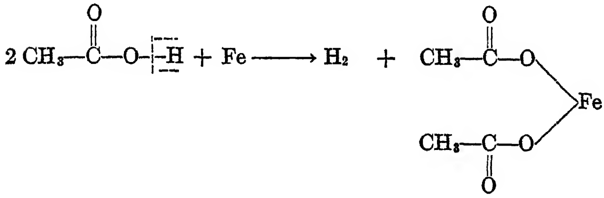
Name	*Formulas*	*Remarks*
The two simplest acids Formic acid or Methanoic acid	$H{-}COOH$ $H{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}H$	This acid was known to the ancients and was obtained from red ants. (Latin, *formica,* or ant.) It occurs in ants, bees, and nettles. The irritation caused by the sting of bees, and perhaps of ants and other insects, is due in part to the injection of this acid under the skin.
Acetic acid or Ethanoic acid	$CH_3{-}COOH$ $CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}H$	This is the chief acid in vinegar. It is a product of the fermentation of sugar to make alcohol which, in time, oxidizes to acetaldehyde; then, as should be expected, to acetic acid.
In fruits and plants Oxalic acid	$\begin{array}{l} COOH \\ \| \\ COOH \end{array}$ $\begin{array}{l} O \\ \| \\ C{-}O{-}H \\ \| \\ C{-}O{-}H \\ \| \\ O \end{array}$	Oxalic acid, together with its salts, is widely distributed in leaves and fruits of plants. The sour taste of some leaves, such as the sorrel, is due to its presence. It is the strongest of the organic acids. It is a good reducing agent. Perhaps its poisonous effect, also its use as a bleach and stain remover, is due to one or the other of these properties.
Malic acid	$\begin{array}{l} COOH \\ \| \\ CH_2 \\ \| \\ CHOH \\ \| \\ COOH \end{array}$	Malic acid is widely distributed in fruits — in apples, pears, grapes, strawberries, and other fruits.
Tartaric acid	$\begin{array}{l} COOH \\ \| \\ CHOH \\ \| \\ CHOH \\ \| \\ COOH \end{array}$	It is interesting to note the chemical relationship between tartaric and malic acids. Both are dicarboxylic, and both are derivatives from butane. Both are also secondary alcohols, malic acid with one such group, tartaric acid with two. Tartaric acid occurs in fruits and is especially abundant in grapes.

Name	*Formulas*	*Remarks*
In fruits and plants *(cont.)* Citric acid	COOH | CH_2 | HO—C—COOH | CH_2 | COOH	This acid derives its name from its occurrence in citrous fruits, notably in lemons, its chief commercial source. It is widely distributed in fruits, including lemons, limes, gooseberries, and currants.
Fatty acids		
Butyric acid	C_3H_7—COOH	These acids are made from the hydrolysis of the fats butyrin, palmitin, stearin, and olein respectively (p. 369). They are made as digestive products of fats in the intestine, and as hydrolysis products in the cells. Butyric acid is present in rancid butter, in cheese, and in perspiration. It has an unpleasant odor.
Palmitic acid	$C_{15}H_{31}$—COOH	
Stearic acid	$C_{17}H_{35}$—COOH	
Oleic acid	$C_{17}H_{33}$—COOH	
Other acids of physiological importance		
Lactic acid	CH_3 | CHOH | COOH	Lactic acid, derived from lactose, is a component of sour milk. All three of these acids appear in the cells as intermediate compounds in the metabolic series of reactions. *Lactic acid* is made during the metabolism of glucose (p. 467). *β-hydroxybutyric acid* and *diacetic acid* are made in the fatty acid oxidation series of reactions; and when fat metabolism is faulty they are excreted in the urine (p. 474).
β-hydroxybutyric acid	CH_3 | CHOH | CH_2 | COOH	
Diacetic acid or Acetoacetic acid or β-oxybutyric acid	CH_3 | CO | CH_2 | COOH	

As acids with metals above hydrogen. Organic acids react with metals above hydrogen to make hydrogen and salts. Accordingly, acetic and tartaric acids react with iron, as should be anticipated, yielding products as specified in the following:

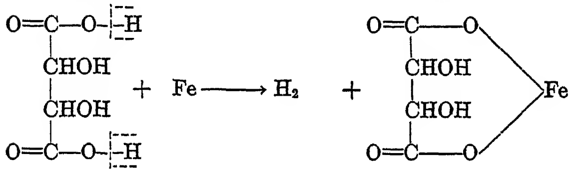
Acetic acid + Iron → Hydrogen + Ferrous acetate

$$2\,HC_2H_3O_2 + Fe \longrightarrow H_2 + Fe(C_2H_3O_2)_2$$



Tartaric acid + Iron → Hydrogen + Ferrous tartrate

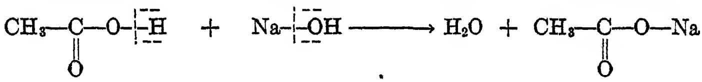
$$H_2C_4H_4O_6 + Fe \longrightarrow H_2 + FeC_4H_4O_6$$



As acids with bases. Organic acids react with bases to make water and salts. Thus in specific application:

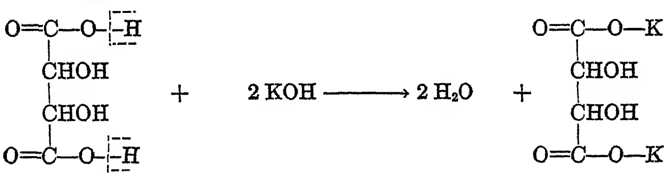
Acetic acid + Sodium hydroxide → Water + Sodium acetate

$$HC_2H_3O_2 + NaOH \longrightarrow H_2O + NaC_2H_3O_2$$



Tartaric acid + Potassium hydroxide → Water + Potassium tartrate

$$H_2C_4H_4O_6 + 2\,KOH \longrightarrow 2\,H_2O + K_2C_4H_4O_6$$



As acids with alcohols. But if the base is an alcohol, then the organic acid reacts with said alcohol to make water and a salt which is an *ester* (p. 340). When applied to the foregoing acids with ethyl alcohol, reactions occur as represented below:

Acetic acid + Ethyl alcohol → Water + Ethyl acetate

$$CH_3\text{—}COO\text{-}H + C_2H_5\text{-}OH \rightarrow H_2O + CH_3COO\text{—}C_2H_5$$

Tartaric acid + Ethyl alcohol → Water + Ethyl tartrate

$$\begin{array}{l} COO{-}H \\ | \\ CHOH \\ | \\ CHOH \\ | \\ COO{-}H \end{array} + 2\,C_2H_5{-}OH \rightarrow 2\,H_2O + \begin{array}{l} COO{-}C_2H_5 \\ | \\ CHOH \\ | \\ CHOH \\ | \\ COO{-}C_2H_5 \end{array}$$

As acids with metal oxides. Organic acids can also be expected to react with metal oxides to make water and salts. Therefore, again using acetic and tartaric acids as examples and with ferric oxide, reactions should take place as follows, but this time, let us revert to formulas after the inorganic method for representing these acids and salts:

Acetic acid + Ferric oxide → Water + Ferric acetate

$$6\,HC_2H_3O_2 + Fe_2O_3 \longrightarrow 3\,H_2O + 2\,Fe(C_2H_3O_2)_3$$

Tartaric acid + Ferric oxide → Water + Ferric tartrate

$$3\,H_2C_4H_4O_6 + Fe_2O_3 \longrightarrow 3\,H_2O + Fe_2(C_4H_4O_6)_3$$

Reactions from all of the foregoing contacts with organic acids are of vast importance: they are studied and used in laboratories; they are of considerable consequence in manufacturing concerns; and some are commonly met with in everyday procedures, especially in the field of food preparations. Reactions do follow from contacts of acid components of food mixtures with the aluminium or the iron of pans or kettles. And it is a well-known fact that foods which contain acids "clean" the collection of iron rust (ferric oxide) or aluminium rust (aluminium oxide) from utensils thus rusted. But this subject received some detailed attention in a previous discussion (Chapter XV), a review of which should be profitable.

FATTY ACIDS

Representative fatty acids. Fatty acids result from the hydrolysis of fats. Those of most common mention are butyric, palmitic, stearic, and oleic acids; but there are others, including valeric, caproic, linoleic, and linolenic acids. The last two fatty acids mentioned are made from the hydrolysis of fat components present

in linseed oil. Two of the various formula representations for these fatty acids are as follows:

Name	*Formula stressing carboxyl group*	*Semistructural formula for molecule*
Saturated fatty acids:		
Butyric acid	C_3H_7COOH	$CH_3—CH_2—CH_2—COOH$
Valeric acid	C_4H_9COOH	$CH_3—CH_2—CH_2—CH_2—COOH$
Caproic acid	$C_5H_{11}COOH$	$CH_3—CH_2—CH_2—CH_2—CH_2—COOH$ or more briefly $CH_3—(CH_2)_4—COOH$
Palmitic acid	$C_{15}H_{31}COOH$	$CH_3—(CH_2)_{14}—COOH$
Stearic acid	$C_{17}H_{35}COOH$	$CH_3—(CH_2)_{16}—COOH$
Unsaturated fatty acids:		
Oleic acid	$C_{17}H_{33}COOH$	$CH_3(CH_2)_7—CH{=}CH—(CH_2)_7—COOH$
Linoleic acid	$C_{17}H_{31}COOH$	Two sets of two carbon atoms joined with double bonds.
Linolenic acid	$C_{17}H_{29}COOH$	Three sets of two carbon atoms joined with double bonds.

The term *fatty acids* is applied not only to acids that are made by the hydrolysis of fats but also to *all acids of the open-chain saturated series* to which most of these fatty acids belong. Thus, formic acid and acetic acid, chemically related to butyric, palmitic, and stearic acids, are likewise called fatty acids, although they are not products of the hydrolysis of fats.

Chemical behavior as acids. All of the fatty acids specified, although weak electrolytes, are capable of yielding appreciable concentrations of hydrogen ions. Also, as acids, they react with bases and alcohols according to rule (p. 331). From a commercial angle it is as the result of reactions of fatty acids with bases that soaps are made (p. 339). From a physiological viewpoint it is through reactions of such acids with glycerol, as an alcohol, that body fats are made (p. 470).

As saturated or unsaturated fatty acids. *Factually,* whether a fatty acid, or any other organic acid, is saturated or unsaturated depends entirely upon its hydrocarbon part. If this hydrocarbon is saturated (p. 294), then the fatty acid is called a saturated fatty acid; but if the hydrocarbon part of the acid is unsaturated, then the fatty acid is regarded as being unsaturated. (See above semistructural formulas; also consult formulas on pp. 367–368). Accordingly:

Butyric acid, Valeric acid, Caproic acid, Palmitic acid, Stearic acid } are saturated because, supposedly, all carbon atoms within the molecules are joined with single bonds, hence there are no available bonds for reaching out to combine with other elements.

Oleic acid, Linoleic acid, Linolenic acid } are unsaturated because, according to belief, one or more pairs of carbon atoms within their molecules are joined with double bonds. Therefore, at points where double bonds occur, direct combination with hydrogen atoms, or atoms of other elements, is possible. Of course when this happens the double bond between carbon atoms gives way to a single bond and the hydrocarbon part of the molecule, hence the fatty acid molecule as a whole, becomes saturated. Such a reaction between oleic acid and hydrogen is represented as follows:

$$\overbrace{CH_3{-}(CH_2)_7{-}\underset{H}{\underset{|}{C}}{=}\underset{H}{\underset{|}{C}}{-}(CH_2)_7{-}COOH}^{\substack{\textit{Oleic acid}\text{ (unsaturated)}\\ C_{17}H_{33}COOH}} + H_2 \rightarrow \overbrace{CH_3{-}(CH_2)_7{-}\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}{-}\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}(CH_2)_7{-}COOH}^{\substack{\textit{Stearic acid}\text{ (saturated)}\\ C_{17}H_{35}COOH}}$$

The chief importance of these two varieties of fatty acids is in respect to fats, because fats are saturated or unsaturated (pp. 367–368) depending upon whether their fatty acid radical constituents are saturated or unsaturated. And the contrasting chemical behavior of these two varieties of fats have a significant bearing in everyday concerns, including some of physiological interest (p. 370).

AMINO ACIDS

What is an amino acid? Among the various substitution products on organic acids that are of vital importance are the amino substitutes commonly called amino acids. The *amino* is a derivative of ammonia (NH_3),[1] hence, its name. It has a composition and valence as is indicated in its formula $—NH_2$; its atom group accordingly has a supposed composition and structure represented thus:

Amino atom group (*structural and empirical formulas*)

$$-N\begin{matrix}\diagup H\\ \diagdown H\end{matrix} \qquad\qquad -NH_2$$

[1] Another radical derived from ammonia is called *imino*. Its formula and valence are represented thus: $>NH$.

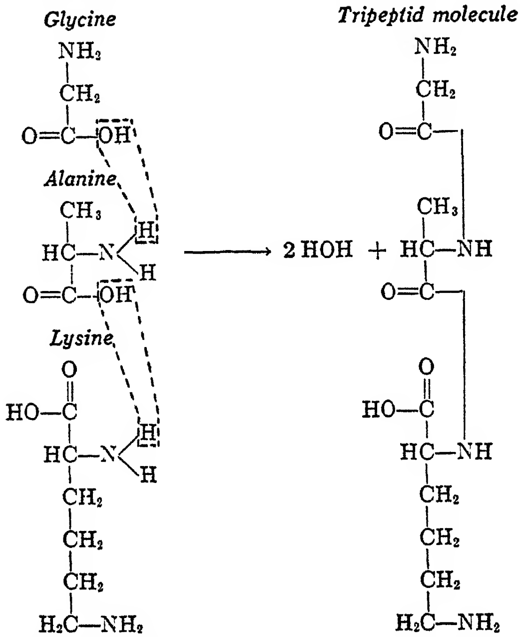
It would follow, therefore, that the molecule of every amino acid must contain both a carboxyl and an amino atom group as is indicated in the semistructural formulas for the amino acids listed in the following table (see also pp. 416–417). In the structural name for each of these acids, *alpha* (α) *amino* signifies that the amino group is substituted on the carbon atom that is *next to the carboxyl.*

Common name	*Structural name*	*Formula*
Glycine	Alpha(α)-amino acetic acid	$\begin{array}{l} NH_2 \\ \vert \\ CH_2—COOH \end{array}$
Alanine	Alpha(α)-amino propionic acid	$\begin{array}{lll} & NH_2 & \\ & \vert & \\ CH_3— & CH & —COOH \end{array}$
Cystine	An alpha(α)-amino derivative of two molecules of propionic acid. It is also an important sulfur derivative.	$\begin{array}{lll} & NH_2 & \\ & \vert & \\ CH_2— & CH & —COOH \\ \vert & & \\ S & & \\ \vert & & \\ S & & \\ \vert & & \\ CH_2— & CH & —COOH \\ & \vert & \\ & NH_2 & \end{array}$
Lysine	Alpha(α)-epsilon(ϵ)-diamino caproic acid	$\begin{array}{lllll} NH_2 & & & & NH_2 \\ \vert & & & & \vert \\ CH_2— & CH_2— & CH_2— & CH_2— & CH—COOH \end{array}$
Isoleucine	Alpha(α)-amino, beta(β)-methyl valeric acid	$\begin{array}{llll} & & CH_3 & NH_2 \\ & & \vert & \vert \\ CH_3— & CH_2— & CH— & CH—COOH \end{array}$

Chemical behavior. Of the three chemical reactions common to amino acids which are presented in this study, one is *believed* to take place, the other two are *known* to occur.

Amino acids dehydrolyze to make proteins. It is *believed* that various animal cells select specific amino acids from among those brought to them by the blood stream and subject them to the process of dehydrolysis to make cell proteins of their own peculiar character. Presumably, during dehydrolysis, hydroxyl atom groups are taken from carboxyls and hydrogen atoms from aminos of adjacent amino acids to make molecules of water, and the

amino acids thus rendered incomplete combine with each other at these evacuated points to make the protein molecules. Such a combination between three amino acid molecules is represented in the following; in the making of a protein molecule, hundreds of amino acids are believed to become thus involved:



Amino acids with bases. Through their carboxyls and due to replaceable hydrogens in the same, amino acids react in the usual manner with bases to make *water* and *salts*. Thus in respect to molecules of alanine and sodium hydroxide:

Alanine + Sodium hydroxide ⟶ Water + Sodium alanate

$$CH_3-\underset{}{\overset{NH_2}{\overset{|}{C}H}}-COO\,\boxed{H} + Na\,\boxed{OH} \longrightarrow H_2O + CH_3-\overset{NH_2}{\overset{|}{C}H}-COONa$$

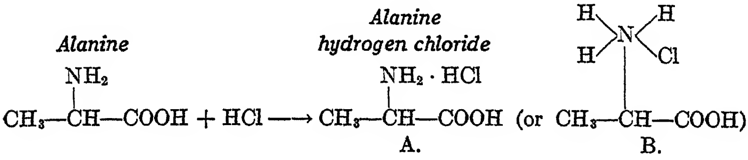
As nitrogen bases with acids. A fact that has not come to the attention until now is that the amino group, regardless of what compound it may be a constituent, enters into direct combination with an acid. It is for this reason that compounds containing the amino are frequently referred to as *nitrogen bases*, since through the agency of their amino groups acids are destroyed.[2]

[2] Either the amino ($-NH_2$) or imino ($>NH$) atom group is a constituent of every alkaloid molecule and accounts for its behavior as a nitrogen base in reaction with acids. It is this behavior that gives rise to the class label of *alkaloids*.

So it is that amino acids are nitrogen bases and combine with other acids to destroy them. Examples are as follows:

Alanine + Hydrochloric acid → Alanine hydrogen chloride
Glycine + Sulfuric acid ⟶ Glycine hydrogen sulfate

As to the manner in which the amino atom group combines with an acid there is uncertainty of opinion. However, the following is a venture at representing what may possibly occur, using alanine and hydrochloric acid molecules as characteristic reacting parties:



A. This represents a combination with the other acid at the amino within the molecule of the amino acid but does not venture a suggestion as to the manner of combination.
B. This is more venturesome and suggests that during combination the valence of the nitrogen atom may be increased from three to five.

Amino acids are amphoteric, meaning that they have a double nature: (1) through their carboxyls they are acids, hence they react with bases; (2) through their aminos they react with other acids. And herein lies the reason for one of the vital functionings of amino acids in body cells, lymph, and blood (p. 501) where, because of their double reacting capacity with bases and acids, they become one of the mechanisms through which the hydrogen ion and hydroxyl ion concentrations in these regions is maintained within the range, a little on the basic side, which is vital to the living, healthy animal.

ORGANIC SALTS AND ESTERS

Organic salts, classification. Salts that are composed of metal or ammonium radicals in combination with organic acid radicals are classed as *organic salts*. This is in contrast with the other type of organic salts that contain hydrocarbon radicals as metal-acting radicals, which are *esters*. The following are examples of organic salts in contrast with some esters, together with formulas for the same both after the inorganic manner and, semistructurally, after the organic manner:

Organic salts			Esters		
Sodium acetate	$NaC_2H_3O_2$	$CH_3—COONa$	Methyl chloride	CH_3Cl	$CH_3—Cl$
Ammonium oxalate	$(NH_4)_2C_2O_4$	$COO—NH_4$ | $COO—NH_4$	Ethyl acetate	$C_2H_5C_2H_3O_2$	CH_3 | $COO—C_2H_5$
Potassium tartrate	$K_2C_4H_4O_6$	COOK | CHOH | CHOH | COOK	Glyceryl stearate	$C_3H_5(C_{17}H_{35}CO_2)_3$	See pp. 367–368
			Glyceryl nitrate	$C_3H_5(NO_3)_3$	$CH_2—NO_3$ | $CH—NO_3$ | $CH_2—NO_3$

Organic salts, chemical behavior. Organic salts react chemically as do all salts. Among such possibilities are the following:

They are strong electrolytes, hence when in water solution they are ionized. In respect to sodium acetate and ammonium oxalate in water solution, reactions as electrolytes are represented as follows:

$$\begin{array}{cccc} \text{Sodium acetate (undissociated)} & \longrightarrow \text{Sodium ions} & + & \text{Acetate ions} \\ NaC_2H_3O_2 & \longrightarrow Na^+ & + & C_2H_3O_2^- \end{array}$$

$$\begin{array}{cccc} \text{Ammonium oxalate (undissociated)} & \rightarrow \text{Ammonium ions} & + & \text{Oxalate ions} \\ (NH_4)_2C_2O_4 & \longrightarrow 2\,NH_4^+ & + & C_2O_4^{--} \end{array}$$

Organic salts react with acids according to expectation, namely:

$$\text{Salt} + \text{Acid} \longrightarrow \text{Salt} + \text{Acid}$$

Such a reaction between sodium acetate and sulfuric acid is, therefore, as follows:

$$\begin{array}{ccccc} \text{Sodium acetate} & + \text{ Sulfuric acid} & \rightarrow \text{Sodium sulfate} & + & \text{Acetic acid} \\ 2\,CH_3COONa & + \ H_2SO_4 & \longrightarrow Na_2SO_4 & + & 2\,CH_3COOH \end{array}$$

Organic salts readily undergo hydrolysis. For example:

$$\begin{array}{ccccccc} \text{Ammonium oxalate} & + & \text{Water} & \longrightarrow & \text{Ammonium hydroxide} & + & \text{Oxalic acid} \\ \begin{array}{l} COO—NH_4 \\ | \\ COO—NH_4 \end{array} & + & 2\,HOH & \longrightarrow & 2\,NH_4OH & + & \begin{array}{l} COO—H \\ | \\ COO—H \end{array} \end{array}$$

$$\begin{array}{ccccccc} \text{Potassium tartrate} & + & \text{Water} & \longrightarrow & \text{Potassium hydroxide} & + & \text{Tartaric acid} \\ \begin{array}{l} COOK \\ | \\ CHOH \\ | \\ CHOH \\ | \\ COOK \end{array} & + & 2\,HOH & \longrightarrow & 2\,KOH & + & \begin{array}{l} COOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ COOH \end{array} \end{array}$$

Soaps. ***Composition.*** Among the most important of the *organic salts* are soaps. Soaps have for constituents a metal or an ammonium radical in combination with such fatty acid radicals as are present in fats. Here are examples, and at the same time the given soaps are listed as to whether they are of the cleansing or noncleansing variety:

Cleansing soaps		*Noncleansing soaps*	
Sodium stearate	$NaC_{17}H_{35}CO_2$	Calcium stearate	$Ca(C_{17}H_{35}CO_2)_2$
Potassium palmitate	$KC_{15}H_{31}CO_2$	Magnesium palmitate	$Mg(C_{15}H_{31}CO_2)_2$
Sodium oleate	$NaC_{17}H_{33}CO_2$	Zinc stearate	$Zn(C_{17}H_{35}CO_2)_2$

Cleansing soaps. Sodium and potassium soaps are of the cleansing variety. Three examples of such are given in the foregoing list. Sodium soaps are *hard* soaps, while potassium soaps are *soft* soaps. All cleansing soaps give colloidal dispersions (p. 210) with water as is evidenced by the familiar translucent effect produced when a soap and water system is shaken and "suds" appear.

Frequently these colloidal soap-water dispersions are carelessly called solutions (p. 210). As a matter of fact, if soaps did give true solutions with water they would be able automatically to effect distribution as to each other with no need for the effort and time commonly used for rubbing soap into the water. But soaps do form true solutions with alcohol.

Making soaps. Compounds that are used in the making of soaps are fats and either sodium or potassium hydroxide. As for the reactions concerned, it is believed that they take place in two steps: *first,* the fats hydrolyze to make glycerol and fatty acids, the base acting as a catalyst for the reactions; *second,* the fatty acids made react with the base present to make water and the desired soap. With glyceryl stearate as the fat and sodium hydroxide as the base, reactions occur as follows:

$$\text{Glyceryl stearate} + \text{Water} \xrightarrow{\text{Sodium hydroxide}} \text{Stearic acid} + \text{Glycerol}$$
$$C_3H_5(C_{17}H_{35}CO_2)_3 + 3\,HOH \longrightarrow 3\,C_{17}H_{35}COOH + C_3H_5(OH)_3$$

$$\text{Stearic acid} + \text{Sodium hydroxide} \longrightarrow \text{Water} + \text{Sodium stearate (the soap)}$$
$$C_{17}H_{35}COOH + NaOH \longrightarrow HOH + C_{17}H_{35}COONa$$

Frequently, however, these reactions are represented as occurring in only one step (p. 369), between the fat and the base, thus:

$$\text{Glyceryl stearate} + \text{Sodium hydroxide} \longrightarrow \text{Glycerol} + \underset{\text{(the \textit{soap})}}{\text{Sodium stearate}}$$
$$C_3H_5(C_{17}H_{35}CO_2)_3 + 3\,NaOH \longrightarrow C_3H_5(OH)_3 + 3\,C_{17}H_{35}COONa$$

In the actual making of soap, either in the household or commercially, the naturally occurring fats that are used are *fat mixtures* — in the main mixtures of glyceryl stearate, glyceryl palmitate, and glyceryl oleate — hence the resulting soap products are soap mixtures.

In pioneer days soap-making was one of the regular home tasks. Scrap fats were saved up during the year for the spring soap-making. The year's yield of wood ashes was accumulated and "leached" to obtain "potash." Actually, as is now known, potash is largely potassium carbonate which reacts with water to yield potassium hydroxide for the making of the soap. In those days the obtaining of "good soap" was an art, in that favoring proportions as to potash and fat could be arrived at only by numerous trial and error procedures. But today soap-making is on a scientific basis, the difference between the "then" and "now" lying in the fact that today chemists understand the reactions that occur and can compute exact quantities of fat and base to be used and exact quantities of soap product which will result. Thus with glyceryl stearate as the fat and sodium hydroxide as the base the following are typical computations:

$$\underbrace{\overset{\textit{Specific fat}}{C_3H_5(C_{17}H_{35}CO_2)_3}} + \underbrace{\overset{\textit{Specific base}}{3\ NaOH}} \longrightarrow C_3H_5(OH)_3 + \underbrace{\overset{\textit{Specific soap}}{3\ C_{17}H_{35}COONa}}$$

The weight relationship	891.45	120.015	919.371
Hence,	7.42 lbs.	1 lb.	7.66 lbs.

Potassium soaps are *soft soaps* which are good cleansing soaps but not as convenient to use as are sodium or hard soaps that can be moulded into cakes. However, for some special uses potassium soaps are made even now; thus green soap is a mixture of sodium and potassium soaps.

Insoluble soaps do not give colloidal solution with water. Among these are the objectionable calcium and magnesium soaps that are made when soaps react with the salts of hard water (p. 204).

A new detergent. Within the past few years a new type of detergent has been developed that serves most satisfactorily as a cleansing agent. It is not a soap, but is a derivative of sodium sulfate and such hydrocarbons as are obtained from petroleum oil. It can be used in hard as well as soft water and is very speedy in its cleansing action. The future of such soap substitutes seems most promising.

Esters. Esters are salts that contain hydrocarbons as metal-acting radicals in combination with either inorganic or organic

acid radicals. (For examples, see p. 338.) Esters are of widespread occurrence in nature: fats are esters, and the characteristic odors and flavors of flowers and fruits are usually due to the presence of specific esters. For example: ethyl butyrate ($C_3H_7COO — C_2H_5$) is a substance with a pleasant odor present in pineapples; octyl acetate ($CH_3COO — C_8H_{17}$) is a pleasantly odorous component of oranges. In manufacturing concerns numerous esters are made for contributing to various synthetic perfumes and flavors.

Chemical behavior of esters. *They are not electrolytes.* Unlike metallic salts, esters dissociate in water solution to yield ions only to such an exceedingly slight extent that they are classed as nonelectrolytes. As a result, reactions involving esters, as salts, are exceedingly slow unless catalytic aid is provided.

With water in hydrolysis. The only one of the reaction possibilities on the part of esters to which we shall give attention in this study is in respect to their hydrolysis. These reactions are rendered appreciable in the presence of a dilute acid or dilute base functioning as a catalyst. Thus, in brief general statement and with examples:

$$\text{Ester} + \text{Water (in hydrolysis)} \xrightarrow{\text{Base or acid}} \text{Alcohol} + \text{Acid}$$

$$\begin{array}{ccccccc} \text{Ethyl chloride} & + & \text{Water} & \xrightarrow{\text{Base or acid}} & \text{Ethyl alcohol} & + & \text{Hydrochloric acid} \\ C_2H_5Cl & + & HOH & \longrightarrow & C_2H_5OH & + & HCl \end{array}$$

$$\begin{array}{ccccccc} \text{Ethyl acetate} & + & \text{Water} & \xrightarrow{\text{Base or acid}} & \text{Ethyl alcohol} & + & \text{Acetic acid} \\ CH_3COO—C_2H_5 & + & HOH & \longrightarrow & C_2H_5—OH & + & CH_3COO—H \end{array}$$

Such reactions are not new to this study because the first reaction that occurs in soap-making involves the hydrolysis of fats speeded up by the presence of a base (p. 339). Also the reactions which take place in the digestion of fats are hydrolysis reactions speeded up by the presence of the enzyme catalyst steapsin (pp. 450, 452).

Esters of importance. As already stated repeatedly fats are esters in which the hydrocarbon radical is always the glyceryl radical ($C_3H_5^{+++}$), but the fatty acid radicals can vary. Glyceryl butyrate is a component of butter; glyceryl stearate, glyceryl palmitate, and glyceryl oleate are present in mixture in nearly all natural fats. More concerning these fats will be considered later. Their empirical formulas are as follows:

Glyceryl butyrate	$C_3H_5(C_3H_7COO)_3$
Glyceryl stearate	$C_3H_5(C_{17}H_{35}COO)_3$
Glyceryl palmitate	$C_3H_5(C_{15}H_{31}COO)_3$
Glyceryl oleate	$C_3H_5(C_{17}H_{33}COO)_3$

There are esters which have *medicinal uses: ethyl chloride* is a local anesthetic (p. 301); *amyl nitrite* ($C_5H_{11}NO_2$) is prescribed commonly for persons suffering from angina pectoris; *ethyl nitrite* ($C_2H_5NO_2$), sometimes called nitrous ether, is used as a diuretic, its alcoholic solution is called sweet spirits of nitre.

Questions

1. What atom group is typical of such organic acids as are the subject of study in this chapter? Represent both structurally and semistructurally.

2. In what respect is the behavior of organic acids similar to that of inorganic acids? Assemble word and formula equations for typical reactions, with formulas for organic acids and salts given in the organic manner.

3. From the standpoint of the specific organic acid components involved, indicate what reaction, if any, can be expected from each of the following contacts:
   a. Grapes cooked in an aluminium dish.
   b. Apples cooked in an iron kettle.
   c. Bicarbonate of soda used with sour milk in cookery.
   d. Sodium bicarbonate or ammonium hydroxide solution in the treatment of skin irritation caused by nettles or by a bee sting.

4. What are fatty acids? What is their usual source? Name at least six fatty acids. Why are they important physiologically?

5. What is an amino acid? Give examples with formula representations. What is their usual source? Why are they important physiologically?

6. Amino acids are amphoteric. What does this mean? Illustrate by reference to the amino acid lysine, giving formula equations for the reactions.

7. What is an organic salt? Give examples. How does an ester differ from other organic salts: (a) as to composition? (b) as to chemical behavior? (c) Give examples of esters that contain inorganic acid radicals. Organic acid radicals.

8. What is a soap? How are soaps made commercially? Assemble word and formula equations representative of the reactions involved in making (a) a hard soap, (b) a soft soap. With glyceryl stearate as the fat, how much fat and how much sodium hydroxide would be required to make five pounds of soap?

9. Fats are classed as esters. Why? Illustrate with reference to some specific fat.

CHAPTER XXV

Carbohydrates

The carbohydrates as a class of compounds include sugars, starches, and celluloses; they are widely distributed in nature, abundantly so in plants and to a limited extent in animals. *Sugars* are found circulating in all plant fluids; they are relatively concentrated in the juices of some ripe and other unripe fruits and vegetables: in ripe pears, peaches, carrots, and beets, and in "green" or unripe peas, beans, and corn. Sugars are also present in considerable concentration in the saps of sugar cane and the sugar maple. *Starches* are stored in the roots of some vegetables and in the ripened seeds of many plants. The woody structure of trees as well as the supporting fibers of all stems and leaves of plants is largely *cellulose*, and the cotton fiber is relatively pure cellulose. The importance of these carbohydrates of plant origin is recognized when one considers the large part that sugars and starches play in providing the food supply of man and of other animals; and the usefulness of celluloses as fuels, in construction, and in the production of paper, fabrics, and an ever increasing group of useful synthetic materials. Carbohydrates also occur in animals, although less abundantly than in plants. *Glucose*, for example, is found in the blood and lymph, and in actively functioning tissue cells where, as chief among its functions, it serves as a partner for oxygen in producing the energy necessary for living. *Glycogen*, which is related to the starches, is made in animal cells, particularly in those of the liver and muscles, and it is a carbohydrate suitable (p. 350) for storage within said cells.

Composition. Carbohydrates, as their name implies, are composed of the elements carbon, hydrogen, and oxygen; the hydrogen and oxygen usually, though not always, being present in the same proportions as in water, a fact which is indicated by the formulas for glucose ($C_6H_{12}O_6$) and sucrose ($C_{12}H_{22}O_{11}$). From the standpoint of chemical behavior, carbohydrates react in part as primary alcohols and in part as secondary alcohols. This fact has led to the belief that molecules of all carbohydrates must contain both primary and secondary alcohol atom groups; and in addition to

these atom groups all carbohydrate molecules are believed to contain either an aldehyde or a ketone atom group, free or combined. The following semistructural formula for the molecule of *glucose* represents the presence of these characteristic atom groups.

$$\begin{array}{l}
\mathrm{CHO} \longleftarrow \text{An aldehyde atom group.} \\
| \\
\left.\begin{array}{l} \mathrm{CHOH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CHOH} \end{array}\right\} \longleftarrow \text{Four secondary alcohol atom groups.} \\
| \\
\mathrm{CH_2OH} \longleftarrow \text{One primary alcohol atom group.}
\end{array}$$

Synthesis. Carbohydrates are made in the cells of green plants from carbon dioxide obtained from the air and water entering through the roots. Animals lack this ability to build carbohydrates from inorganic materials. This important process of making carbohydrates takes place in the leaves of green plants in the presence of sunlight, hence the name *photosynthesis* has been given to the phenomenon. The exact nature of the reactions which are involved is unknown; nor is it known just what carbohydrate may be made first in the cells or whether this first-made carbohydrate may vary in the cells of different plants or in different cells of the same plant. Chlorophyll, which gives the green color to the leaves, plays an essential part in the reaction and although chemists are not in agreement as to its exact function, it is believed by some that it functions as a catalyst. Sunlight provides energy which within the cells is transformed into the extra chemical energy that is essential chiefly to the oxygen which is made, and perhaps in small part to the carbohydrate product, over and above the chemical energy provided by the initial water and carbon dioxide (p. 101). The following equation represents the reactions involved, regarding glucose to be the carbohydrate made:

$$\text{Carbon dioxide} + \text{Water} \xrightarrow{\text{Chlorophyll}} \text{Glucose} + \text{Oxygen}$$

$$\begin{array}{ccccccccc}
6\,CO_2 & + & 6\,H_2O & \xrightarrow{\hspace{4em}} & & C_6H_{12}O_6 & + & 6\,O_2 \\
\downarrow & & \downarrow & & & \downarrow & & \downarrow \\
\begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + \text{Sunlight} & \rightarrow & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array} & + & \begin{array}{c}\text{Chemical}\\ \text{energy}\end{array}
\end{array}$$

There is no reaction known to man which is of greater importance than this photosynthesis reaction.[1] The carbohydrates that

[1] Gortner, R. A., *Outlines of Biochemistry*, John Wiley and Sons, 1938, p. 474.

plants make are important not only as foods in themselves but they are used by plants for the making of fats and proteins. Moreover, it is by means of this reaction that the oxygen supply of earth's atmosphere is constantly replenished; and without this oxygen life would be impossible. Finally, it is through this reaction, and *only* this reaction, that nature captures some of the energy provided by the sun to store it as chemical energy chiefly in the oxygen made. In this manner the energy of the sun is rendered available by way of oxygen (as chemical energy) for later transformation in the cells into those energies which are essential to life, and outside the body into heat and other desired energies. (See Functions of Oxygen, pp. 78–79.)

Basis for classification. Carbohydrates are classed as monosaccharids, disaccharids, and polysaccharids on the basis of their hydrolysis possibilities.

1. *Monosaccharids* are not subject to hydrolysis.
2. A *disaccharid* is a carbohydrate, *factually,* one molecular weight of which reacts with water in hydrolysis to make *two* molecular weights of monosaccharid; or *theoretically,* one molecule of which reacts with water to make two monosaccharid molecules.
3. A *polysaccharid* is a carbohydrate, *factually,* one molecular weight of which reacts with water in hydrolysis to make *several,* sometimes *many,* molecular weights of monosaccharid; or *theoretically,* one molecule of which reacts with water to make several or many monosaccharid molecules.

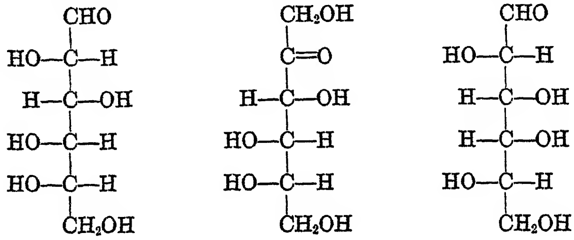
Monosaccharid hexoses. A monosaccharid *hexose* is a carbohydrate one molecular weight of which contains *six* atomic weights of carbon, hence supposedly its molecule contains a chain of *six* carbon atoms. The three monosaccharids which are of special interest to us, namely, *glucose, fructose,* and *galactose,* are of the hexose variety.

There are other monosaccharids than hexoses classed according to the number of atomic weights of carbon known to be present in their molecular weights, hence according to the number of atoms of carbon believed to be present in their molecules. Thus there are bioses, trioses, pentoses, hexoses, etc. Pentoses occur commonly in plant cells.

Both glucose and fructose occur, associated with sucrose, in the juices of fruits and vegetables. Glucose is important because it is the carbohydrate found in circulation in the blood and lymph on its way to the cells of animals, where it performs its vital functions. As far as is known galactose does not occur naturally save as an hydrolysis product of lactose.

All three of these monosaccharids have the same molecular weight and the same element composition as is represented by the same empirical formula, $C_6H_{12}O_6$. Similarities and differences in their chemical behavior are explained as being presumably due to similarities and differences in the arrangement of the atoms within their molecules as represented in the following structural formulas. These formula representations should be studied closely and note made of points within the three molecules wherein they are alike and points wherein they are different.

Glucose *Fructose* *Galactose*

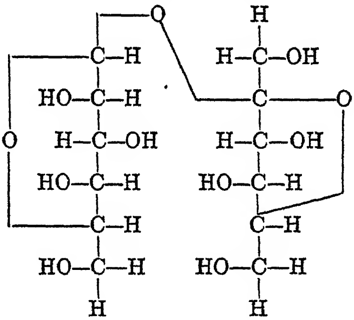
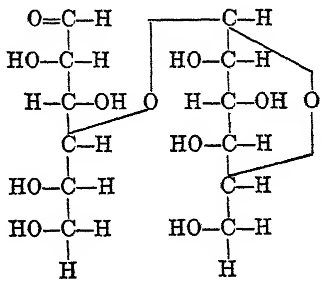


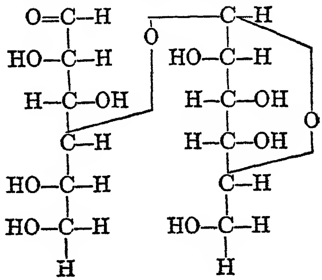
Aside from being both primary and secondary alcohols (p. 307) each of these monosaccharids functions at one point in its molecule either as an aldehyde or as a ketone. For this reason glucose and galactose are sometimes called *aldoses*, meaning sugars which are, in part, aldehydes; whereas fructose is called a *ketose* for a similar reason.

Disaccharid hexoses. ***Occurrence.*** The three important disaccharids are sucrose, maltose, and lactose. *Sucrose* is found in fruit and other plant juices, usually in association with the two monosaccharids glucose and fructose. It is especially abundant in the sap of sugar cane and the sugar beet, and it is from these plants that most of the world's commercial supply of sucrose is obtained. The sugar in the sap of the sugar maple is also largely sucrose. *Maltose* occurs in sprouted grain and it is one of the first products of the hydrolysis of starches (p. 354). *Lactose*, commonly called milk sugar, is of animal origin. It is present in the milk of all mammals and is probably made in the mammary glands.

Composition. As to composition, the same situation is true of these three disaccharids in respect to each other as is true of the three foregoing monosaccharids: namely, they have identical composition as to their molecular weights, a fact that is made evident through their common empirical formula, $C_{12}H_{22}O_{11}$. But they are nonetheless different compounds. Therefore, and again as

with the three foregoing monosaccharids, the chemist turns to the molecules of these three disaccharids and sees there identical numbers of atoms of carbon, hydrogen, and oxygen (empirical formula for molecules $C_{12}H_{22}O_{11}$) but placed differently in some locations in respect to each other. Fortunately there are known facts which give direction to the reasoning guesses as to what these atom placements may be. For example, it is *known* that one molecular weight of sucrose hydrolyzes to make one molecular weight each of glucose and fructose; therefore it is *believed* that the molecule of sucrose is composed of one incomplete molecule of glucose in combination with one incomplete molecule of fructose. Similar reasoning leads to the belief that the maltose molecule is composed of two incomplete, hence combined, molecules of glucose; whereas the molecule of lactose is believed to be composed of combined, incomplete molecules of glucose and galactose. These beliefs as to the molecule structure of these three disaccharids are represented both empirically and structurally as follows:

	Empirical representation	*Structural representation*
A. *Sucrose molecule*	Incomplete glucose molecule · Incomplete fructose molecule $\underbrace{(C_6H_{11}O_6 \cdot C_6H_{11}O_5)}_{C_{12}H_{22}O_{11}}$	
B. *Maltose molecule*	Incomplete glucose molecule · Incomplete glucose molecule $\underbrace{(C_6H_{11}O_6 \cdot C_6H_{11}O_5)}_{C_{12}H_{22}O_{11}}$	

	Empirical representation	*Structural representation*
C. ***Lactose molecule***	Incomplete glucose molecule • Incomplete galactose molecule $\underbrace{(C_6H_{11}O_6 \cdot C_6H_{11}O_5)}_{C_{12}H_{22}O_{11}}$	

For the student a careful study of these structural formulas should show that they represent not only the disaccharid nature of these three carbohydrates and the two combined monosaccharids specifically and respectively concerned, but also the belief that maltose and lactose molecules contain free aldehyde atom groups, whereas the sucrose molecule contains an aldehyde atom group and a ketone atom group but tied up to each other. These latter represented features fit in with the facts, as we shall presently learn, that maltose and lactose do behave chemically as do all aldehydes, whereas sucrose reveals neither its aldehyde nor ketone nature.

Polysaccharid hexosans. The polysaccharids of greatest importance are the starches, dextrins, celluloses, and glycogen. The first three are of plant origin, but glycogen, as far as is known, is the only polysaccharid present in animal cells, particularly in cells of the liver and muscles.

Starches comprise a large portion of the average diet. They are the chief components of grains and from thence appear in bread and cereals. They are components of root vegetables; of ripe corn, peas, and beans; and of unripe fruits. *Dextrins* are intermediate products of the hydrolysis of starches (pp. 353–441). *Celluloses* are the supporting fibers of roots, trunks, stems, and leaves of plants. Consequently, when such foods as lettuce, cabbage, and celery are included in a diet, celluloses in considerable amounts enter the digestive tract as part of the food mixture. However, they are not hydrolyzed by the human animal, possibly because no functioning catalyst is provided, hence in themselves have little food value. But they do serve a purpose in providing the bulk needed for the more efficient peristaltic functioning of the intestine. In the external concerns of man celluloses are exceedingly important: they constitute the greater part of the burnable components of wood; as fibers of cotton and flax they are used for making vari-

ous fabrics; and wood celluloses are used in the manufacture of paper, rayons, lacquers, gun cotton, and many other materials of common use.[2]

The formula $(C_6H_{10}O_5)_n$ represents the composition of all polysaccharids of the hexosan variety. *From a molecular weight viewpoint* this formula means that *one molecular weight* of a polysaccharid hexosan is composed of **n** incomplete molecular weights of a monosaccharid hexose, **n** being a number which varies for the molecular weights of different polysaccharids. Correspondingly, *from the theoretical angle*, this formula means that *one molecule* of a hexosan is composed of **n** incomplete hexose molecules. In the case of the polysaccharids of our chief interest: namely, starches, dextrins, and glycogen — the end product of hydrolysis is the monosaccharid glucose.

There are other polysaccharids which yield other monosaccharids on hydrolysis. For example: pectin, a complex compound present in many fruits and which is responsible for the "setting" of fruit jellies, has as one constituent, a polysaccharid which yields galactose on hydrolysis.

Iodine test for certain polysaccharids. When starches, dextrins, and glycogen are brought in contact with a solution of iodine, certain characteristic color effects are produced which serve as distinguishing tests for these carbohydrates. When starches are in contact with iodine a blue color is obtained. The first dextrins that result from the hydrolysis of a starch give a red-purple to red color when in contact with iodine, consequently these dextrins are known as erythrodextrins (red dextrins). The dextrins that result from the later stages of starch hydrolysis produce no change in color with iodine, hence these dextrins are known as achroodextrins (or without-color dextrins). When glycogen is in contact with iodine in solution a port wine color is obtained. It is not known whether these characteristic color effects are due to a physical or a chemical change on the part of the polysaccharid with the iodine; it is claimed by some to be due to adsorption of the iodine by the polysaccharid.

Concerning some physical properties of carbohydrates. ***Solubilities and diffusion tendencies.*** Both *monosaccharids and disaccharids* form true solutions with water. Such being the case they are subject to osmosis and capable of diffusion through suitable membranes (p. 350); and the distribution of any of these sugars to and from actively functioning cells in either plants or

[2] Lowy and Harrow, *Introduction to Organic Chemistry*, John Wiley and Sons. 1936, p. 187.

animals is dependent upon this property. However, in this connection it is important to note that cells of living membranes often exhibit a selectivity not exhibited by dead membranes; for example, the intestinal membrane permits the diffusion of monosaccharids but not of disaccharids, whereas certain dead membranes are permeable to both of these carbohydrates.

None of the polysaccharids is able to form a true solution with water. *Celluloses* have no tendency whatsoever to enter into either true solution or even into colloidal dispersion with water. *Starch* granules swell considerably in hot water and form either a fine suspension or a colloidal dispersion. This is one of the changes that takes place in the cooking of starches; as a result they are later able to get into larger contact with water in the digesting mass and with the enzymes ptyalin and amylopsin, and are thereby hydrolyzed more speedily. *Dextrins* form colloidal solutions with water. *Glycogen*, when mixed with water and allowed to stand, gradually enters into a more or less lasting colloidal solution.

This inability of polysaccharids to form true solutions and the consequent slight, if any, ability of these carbohydrates to diffuse through membranes (p. 351) is significant in respect to both plant and animal life. Plants store starches in their roots, tubers, and seeds; animals maintain a supply of glycogen in liver and muscle cells; and this is possible because starches and glycogen are not subject to diffusion, hence, cannot escape from said cells.

The differing diffusion tendencies of sugars and polysaccharids can be demonstrated by means of the following experiment. In the apparatus illustrated a dialyzing membrane is securely tied around the end of each of four tubes forming a sack (Fig. 88). Solutions of the sugars glucose and maltose are introduced into sacks A and B, and dispersions of the polysaccharids starch and glycogen into sacks C and D, respectively. Having first made sure that none of the sacks leaks, hence that none of the contents can escape in this manner, each sack is introduced into a beaker of water, as indicated in the diagrams, and allowed to remain for some time, at least an hour. If the dispersed carbohydrate within the sack is able to diffuse through the membrane, in due time it will appear in the water surrounding the sack.

Tests for such diffusion can be made as follows. The solutions in beakers A and B can be tested with Benedict's reagent: if red cuprous oxide is made, thus showing the presence of a reducing sugar, then glucose in A and maltose in B have diffused through the membranes and entered the water surrounding the sacks. Solutions from beakers C and D can be tested with iodine solution; if either starch or glycogen has diffused through the membrane it will produce the usual color effect with the iodine. Repeated experience with such an experiment has failed to show that either of these polysaccharids succeeds in escaping through the membrane into the surrounding water.

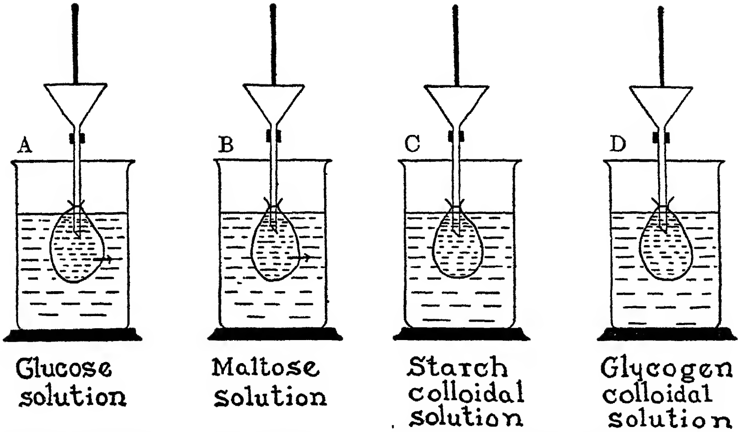


FIG. 88. Sugars can diffuse through membranes, but polysaccharids are not subject to diffusion.

Taste. Solutions of both monosaccharids and disaccharids are more or less sweet; polysaccharids are tasteless. The degree of sweetness of sugars varies with their solubility. Fructose is one of the most soluble of the sugars and it is the sweetest, the extreme sweetness of honey being due to the large proportion of fructose present therein. And everyone is familiar with the ease with which sucrose dissolves in water and also with its sweetness. Lactose is much less readily soluble in water and notably less sweet than sucrose; moreover, it is this lower degree of sweetness of lactose that makes it possible to use it in a relatively large quantity for sweetening a drink when it is desired to increase the caloric value of the beverage without making it unpalatable.

Hydrolysis of disaccharids. As has already been stated, monosaccharids are not subject to hydrolysis as are disaccharids and polysaccharids (p. 345). As for disaccharids, one molecular weight of a disaccharid will react with one molecular weight of water to make two monosaccharid molecular weights (p. 345). Such reactions can be obtained in appreciable proportions by long boiling and are favored by an acid environment; but they take place speedily even at ordinary temperatures through the aid of appropriate enzyme catalysts. For example: the making of boiled frosting and boiled candy involves the hydrolysis of sucrose, and a little vinegar or cream of tartar (potassium hydrogen tartrate) is frequently added to provide the favoring acid environment. The digestion of the disaccharids maltose, sucrose, and lactose involves hydrolysis reactions, with the specific enzymes maltase, sucrase,

and lactase which are provided in the intestinal juice functioning respectively as most effective catalysts.

Word equations for hydrolysis reactions as to disaccharids are given below. These are followed, first by the formula equation, as it usually appears, which functions for any one of the three reactions; then by the equation that indicates the disaccharid nature of these carbohydrates and the hydrolysis nature of the reaction. As to the formula equation, the specific monosaccharids made depend, of course, upon the specific disaccharid that enters the reaction:

$$\text{Sucrose} + \text{Water} \xrightarrow{\text{Sucrase}} \text{Glucose} + \text{Fructose}$$

$$\text{Maltose} + \text{Water} \xrightarrow{\text{Maltase}} \text{Glucose} + \text{Glucose}$$

$$\text{Lactose} + \text{Water} \xrightarrow{\text{Lactase}} \text{Glucose} + \text{Galactose}$$

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 2\ C_6H_{12}O_6$$

$$C_6H_{11}O_6 \cdot C_6H_{11}O_5 + HOH \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

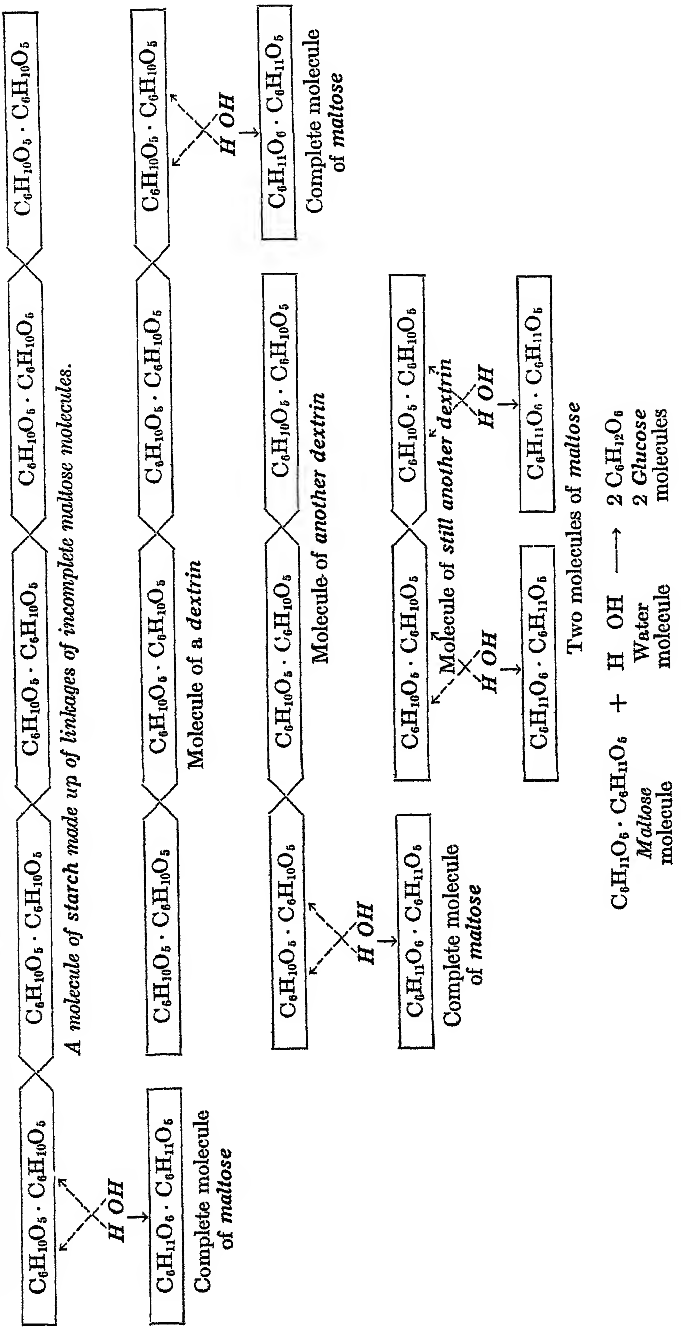
Interpreted. *In large quantity measurements*, and with the dissaccharid as sucrose: one molecular weight of sucrose reacts with one molecular weight of water to make one molecular weight each of glucose and fructose. *Theoretically*, as to the molecule line-up: one molecule of sucrose reacts with one molecule of water to make one molecule each of glucose and fructose.

Polysaccharids also undergo hydrolysis. One molecular weight of each polysaccharid hydrolyzes to make several or many molecular weights of monosaccharid when the reaction is carried to completion. If the polysaccharid is a starch, a dextrin, a cellulose, or glycogen, the monosaccharid is glucose. The equation for any one of these reactions is as follows:

$$(C_6H_{10}O_5)_n + n\ HOH \rightarrow n\ C_6H_{12}O_6$$

The hydrolysis of starch can be brought about by long boiling in an acid environment, a method that is commonly used for making glucose commercially. Starch hydrolysis can also be obtained at ordinary temperatures by the use of exceedingly effective enzyme catalysts called amylases. Ptyalin or salivary amylase and amylopsin or pancreatic amylase are two catalysts of this variety; but starch hydrolysis which is favored by these enzymes carries the reactions only through the dextrin stages to maltose;

A diagrammatic representation of the hydrolysis of a starch molecule



hence for complete hydrolysis, a series of reactions must be obtained as is indicated by the following word equations:

$$\text{Starch} + \text{Water} \xrightarrow{\text{Ptyalin or Amylopsin}} \text{Dextrins} + \text{Maltose}$$

$$\text{Dextrins} + \text{Water} \xrightarrow{\text{Ptyalin or Amylopsin}} \text{Maltose}$$

$$\text{Maltose} + \text{Water} \xrightarrow{\text{Maltase}} \text{Glucose}$$

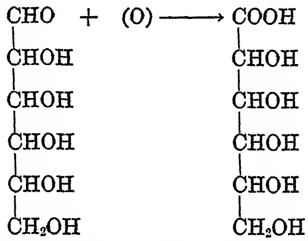
So much is factual, that is, *starch hydrolysis favored by these enzymes does take place through such a series of reactions.*

Now let us turn to the hypothetical starch molecule in an attempt to account for the making of these various products. *First:* supposedly each starch molecule is large and is made up of incomplete glucose molecules; but these glucose molecules are linked in pairs as incomplete maltose molecules, which, in turn, are in combination with each other. *Second:* when hydrolysis of the starch sets in (see diagrammatic representation, p. 353), a water molecule attacks the starch molecule at some point in such a way that a pair of these incomplete glucose molecules breaks off to make a complete maltose molecule, thereby leaving a smaller polysaccharid molecule known as a dextrin. As successive maltose molecules are made in like manner, different and successively smaller dextrin molecules are left, until finally, only maltose molecules are present. *Third:* then, with favoring conditions provided, maltose molecules undergo hydrolysis to make glucose molecules after the manner already presented (pp. 352, 353).

Monosaccharids and disaccharids with oxidizing agents. *Glucose, fructose, galactose, maltose,* and *lactose* all react readily with oxidizing agents, hence they in turn are good reducing agents. When such reactions do take place a small amount of energy product is made, but nowhere nearly as much energy as when these carbohydrates react with oxygen, the substance. That these monosaccharids and disaccharids do react with oxidizing agents is evidenced in the laboratory by the fact that they reduce readily such oxygen-containing compounds as cupric hydroxide, silver oxide, and potassium permanganate. *Sucrose, dextrins, starches,* and *glycogen* are poor reducing agents, hence they reduce the abovementioned oxidizing agents either very, very slowly or apparently not at all.

To explain this differing behavior on the part of the abovementioned carbohydrates one must turn to the supposed make-up of their molecules. Of these carbohydrates, the *good* reducing agents: glucose, galactose, maltose, and lactose, are supposed to

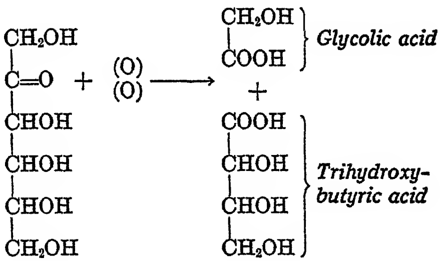
have *free aldehyde* atom groups in their molecules, and each fructose molecule is supposed to contain a *free ketone* atom group; and it is at the free aldehyde and free ketone atom groups that the oxidative attacks on the molecules are believed chiefly to take place. For example, when glucose is oxidized to gluconic acid, it is believed that the aldehyde atom group of the glucose molecule is oxidized to make a carboxyl atom group, hence the gluconic acid molecule. This is represented as follows:



Glucose molecule *Gluconic acid molecule*

When fructose is oxidized, glycolic acid and trihydroxybutyric acid are made, hence the oxidative attack on the fructose molecule is supposed to take place after the following manner:

Fructose



Since sucrose, dextrins, starches, and glycogen are *not* good reducing agents, it is believed that their molecules contain *bound* aldehyde or ketone atom groups (p. 347). These groups then, being bound, are not easily subject to oxidative attack.

No doubt the thoughtful student will have observed the possibility of an oxidative attack at one or more of the alcohol atom groups of the carbohydrate molecules to make aldehydes or ketones. Such attacks are probably possible, but experimental evidence seems to indicate that the aldehyde and ketone groups of the molecule are most vulnerable in this respect.

These oxidation-reduction reactions involving carbohydrates proceed most favorably in an alkaline environment.

Laboratory use of these reactions. Oxidation-reduction reactions in respect to carbohydrates are used in the laboratory as aids in detecting the presence of reducing sugars. Various oxidizing agents are employed for this purpose but the one most frequently used is cupric hydroxide, provided through the agency of either Fehling's or Benedict's reagent. This oxidizing agent is of special interest in the pathological laboratory where it is used in urinalysis to detect the possible presence of glucose. And since both Fehling's and Benedict's reagents are in common use in this connection we will interrupt our main discussion at this point in order to consider similarities and differences as to these two reagents.

Cupric hydroxide presents difficulties for the chemist because it is unstable and also difficult to keep in solution. These difficulties have been circumvented through somewhat different means in these two reagents.

Fehling's reagent was the one first used (p. 318). It is made up of two solutions, Fehling's I and Fehling's II, which are kept separate until immediately before use. Fehling's I contains cupric sulfate which is blue. Fehling's II contains either sodium or potassium hydroxide and Rochelle salt (sodium potassium tartrate) both of which are colorless. Cupric hydroxide is made when the two solutions are mixed; Rochelle salt helps to keep it in solution:

$$\begin{matrix}\text{Cupric} \\ \text{sulfate}\end{matrix} + \begin{matrix}\text{Sodium} \\ \text{hydroxide}\end{matrix} \longrightarrow \begin{matrix}\text{Cupric} \\ \text{hydroxide}\end{matrix} + \begin{matrix}\text{Sodium} \\ \text{sulfate}\end{matrix}$$

$$CuSO_4 + 2\,NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

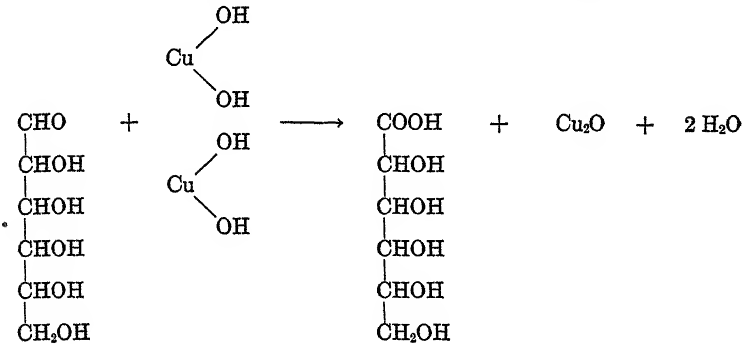
The use of the strong base, sodium hydroxide, provides the favoring and pronounced basic environment.

Benedict's reagent is a modification of Fehling's. It has the advantages of being more stable and of having all reagents in one solution. It provides cupric hydroxide but in a less basic environment. Under the conditions obtained with Benedict's reagent, cupric hydroxide is considered to be more sensitive to reduction by glucose than when obtained from Fehling's reagent. In making Benedict's solution sodium citrate, sodium carbonate, and cupric sulfate are used. There seems to be no certainty as to the exact series of reactions that take place but the following are possibilities. The sodium carbonate may hydrolyze to make a very dilute solution of sodium hydroxide, which in turn may react with the cupric sulfate to make cupric hydroxide, with the sodium citrate as an aid in keeping the cupric hydroxide in solution.

The *cupric hydroxide* thus made by either of these solutions is especially useful as an oxidizing agent, not only because it is easily reduced, but, also, because the product of the reduction is made visible due to its characteristic red color. This product is *cuprous oxide.*

The following equation represents the presumed molecule involvement when cupric hydroxide is reduced by glucose:

Glucose + Cupric hydroxide ⟶ Gluconic acid + Cuprous oxide + Water
(blue) (red)



But it should be remembered that reducing agents other than glucose can produce a similar reaction; therefore, this is not a specific test for the presence of glucose. And, as a matter of fact, other reducing agents than glucose may at times be present in the urine; for example, during the period of lactation, lactose is frequently present in the urine of a nursing mother and the same visual effects will appear in the course of its reaction with cupric hydroxide as with glucose. However, in the main, glucose is the one reducing agent which is likely to be present in urine in quantities sufficient to produce conspicuous effects. The use of formaldehyde as a preservative for urine to be tested for glucose is contraindicated because it is also a good reducing agent (p. 277).

The *quantitative test for blood sugar* is another laboratory procedure which makes use of the fact that glucose is a good reducing agent. In this test provision must be made for measuring accurately the quantity of cupric hydroxide reduced, since a given weight thus reduced is index of a given quantity of glucose present in the volume of blood tested.

With reducing agents. These monosaccharids and disaccharids, again with sucrose excepted, are subject to reduction as well as to oxidation. If aldehydes, they can be reduced to make primary alcohols, or if ketones, to make secondary alcohols. In the process of reduction there is no energy product, but on the contrary some form of energy must be provided to make such reactions possible. Physiologically, it is probable that in the cells in the course of metabolism mutual reduction-oxidation reactions are of frequent occurrence. It is certain that when fat is made from glucose in the cells of the body the reaction involves a reduction of glucose; but

at the same time an oxidation of glucose may be going on in the same cells, perhaps to provide the energy necessary for the above-mentioned reduction.

Fermentation. The three monosaccharids of our study are all subject to fermentation, meaning that they undergo a decomposition which is favored by the presence of certain enzyme catalysts, called ferments or zymases, which are made in the cells of plants, animals, or bacteria. Bread yeast provides one such zymase for the decomposition of glucose, fructose, and galactose to make carbon dioxide and ethyl alcohol. Fructose and glucose are readily subject to this fermentation favored by this zymase, but galactose very much less so. The following equation represents the reaction which takes place when any one of these three monosaccharids undergoes this particular fermentation reaction:

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2\,CO_2 + 2\,C_2H_5OH$$

However, carbon dioxide and ethyl alcohol are not the products of all fermentation reactions; from many such, notably fermentations that are catalyzed by zymases produced in bacterial cells (p. 457), various acids are made.

Disaccharids and polysaccharids are not in themselves subject to fermentation; but if catalysts are provided which favor their hydrolysis, the monosaccharid products of said hydrolysis can then undergo fermentation, conditions being favorable.

Importance of fermentation of monosaccharids. Certain fermentation reactions are of considerable importance *commercially.* For its many practical uses, or as a desired component of beer and ale, ethyl alcohol is obtained from the fermentation of glucose made previously from starch hydrolysis, the zymase for speeding up this fermentation being provided in the appropriate yeast applied. (For word equations concerned, see p. 60.) In making acetic acid of cider-vinegar, the fermentation of glucose and fructose, present in apple juice, produces ethyl alcohol which, in turn, is oxidized to make the acetic acid; zymase for this fermentation is provided by yeast cells of so-called "mother," a brown jelly-like mass which appears whenever vinegar stands for any length of time.

In *household concerns,* the carbon dioxide which is desired for "leavening" of bread dough is a product of fermentation of the monosaccharid glucose, made previously from hydrolysis of the starch component of flour, as well as from glucose and fructose made from the sucrose introduced. The bread yeast contains not

only the enzyme, zymase, for speeding up this fermentation of fructose and glucose but, also, the enzymes maltase and sucrase for their own specific duties; an amylase is provided in the flour. Word equations for this series of reactions involved in the above are given on p. 60; the student should now be able to assemble formula equations for these reactions.

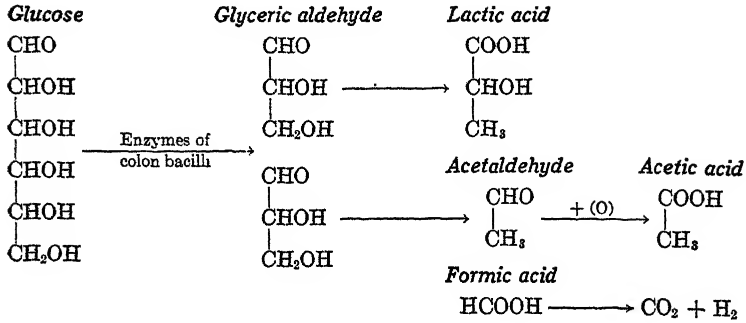
There is no lactase in bread yeast; therefore, lactose cannot undergo hydrolysis through the agency of bread yeast to make monosaccharids, consequently, no fermentation can follow. But there are other yeasts which do contain a lactase along with a zymase; hence, such yeasts are useful for making ethyl alcohol (and carbon dioxide) from the lactose in milk. Thus are obtained the "fermented liquors" of milk origin, koumiss from mare's milk being one such.

The spoilage or "working" of preserved fruits is due to the fermentation of glucose and fructose components therein, the zymase being made in this instance in bacterial or yeast cells which have not been destroyed by adequate sterilization.

Monosaccharid fermentations are also of *physiological importance.* A certain amount of fermentation of monosaccharids is normal in the intestinal tract, the zymases concerned being provided by bacteria normally present. Since a basic environment is favorable to these reactions, it follows that the large intestine is the location of maximum fermentation. Bacillus acidophilus is sometimes prescribed to check excessive intestinal fermentation. The explanation for this effect is that this bacillus secretes a zymase which favors a fermentation involving lactose, one of the products being *lactic acid;* and this acid, in turn, increases the acidity of the intestinal contents thereby rendering the environment less favorable to such fermentation reactions as take place in the more basic medium.

In bacteriology. Many fermentation reactions that are catalyzed by various enzymes produced within bacterial cells are quite specific both as to the particular monosaccharid affected and as to substances made. This selectiveness is frequently resorted to in the laboratory as an aid in the recognition of the particular microorganism producing the enzyme. For example: organisms of the colon bacilli group are known to favor the fermentation of glucose with the production of hydrogen, carbon dioxide, and a number of organic acids. The nature of the reactions concerned is suggested in the following equations:[3]

[3] Salle, A. J., *Fundamental Principles of Bacteriology,* McGraw-Hill Book Co., 1939, pp. 314–316.



Dehydrolysis of monosaccharids for making storage carbohydrates. Nature has provided for the storage of carbohydrates in the form of certain polysaccharids in both plant and animal cells. Various starches found in seeds and in tubers of plants provide a food supply for the young plant. As for animals, the polysaccharid stored within liver cells and utilized in muscle cells is glycogen. It is believed that these polysaccharids are made from monosaccharids in both plant and animal cells by the removal of water, possibly the reverse of the hydrolysis reaction by which monosaccharids are made from polysaccharids (p. 353). This reaction might therefore be called *dehydrolysis*. It can be represented by the following equation:

$$n\ C_6H_{12}O_6 - n\ H_2O \rightarrow (C_6H_{10}O_5)_n$$

Physiological importance of carbohydrates. Statements as to the important part that certain carbohydrates play in animal physiology have been presented from time to time in the previous discussion. The greater part of our food mass is made up of starches; and sugars, to a less extent, are part of the normal diet. But neither starches nor disaccharid sugars can be absorbed from the digestive tract; consequently, they must undergo digestive reactions to make monosaccharids which can be absorbed. The most important of these monosaccharids is glucose which gets carried to the cells where it, together with glycogen made from it, carries on its important functionings. A study of these digestive reactions and the subsequent fate of glucose and glycogen in the metabolic processes will form a part of our future study.

Questions

1. What varieties of compounds belong to the class of carbohydrates? What atom groups are believed to be characteristic of carbohydrate molecules?
2. What is the source of plant carbohydrates? Of animal carbohydrates?

3. What is the so-called "photosynthesis reaction"? Where does it take place? Why is it regarded as one of the most important reactions in all nature?

4. What is the basis for the classification of carbohydrates as monosaccharids, disaccharids, and polysaccharids? Name at least three carbohydrates belonging to each class. Give the empirical formulas for: (a) all monosaccharid hexoses, (b) all disaccharid hexoses, and (c) all hexosans.

5. Assemble word and formula equations for the reactions involved in the hydrolysis of sucrose, lactose, and maltose. How are these reactions made appreciable (a) in cookery, (b) in the digestive tract?

6. a. Indicate by a series of word equations the reaction steps involved in the complete hydrolysis of a starch.
   b. If iodine and Benedict's tests are used to trace the progress of such reactions, what visual evidence would you expect to obtain of these various reaction stages?

7. What is meant by glucose as this term is used commercially? (Consult the United States Pharmacopoeia or any good encyclopedia for this information.) How does commercial glucose differ from the compound glucose? Is there any valid objection to the use of commercial glucose in the preparation of foods, candy, etc.? Give reasons for your answer.

8. What is the common substance provided by both Fehling's and Benedict's reagents? In what respects do the two reagents differ? Which of the carbohydrates of our study give a positive response with these reactions? Which give no response? Account, theoretically, for these different behaviors. Assemble word and formula equations (using semistructural formulas) for the reaction involving glucose.

9. a. Is Fehling's or Benedict's test, either of which is used to detect the presence of glucose in urine, a specific test for glucose? Give reason.
   b. What substance that is commonly encountered in the urine of a nursing mother gives a positive test with either Fehling's or Benedict's reagent? What further test can be made to distinguish this substance from glucose? Give reason.

10. Why is lactose sometimes substituted for sucrose as a sweetening agent in drinks when a high caloric intake is desired?

11. Why do carbohydrates have such an important place in the diet of the average American family? On what grounds is a liberal use of carbohydrate foods justifiable? What, if any, objections are there to such a diet?

12. Account for the fact that, whereas monosaccharids and disaccharids can diffuse through membranes, polysaccharids cannot. Of what advantage is it to the plant or animal to make a carbohydrate of the polysaccharid variety? Do all monosaccharids and disaccharids diffuse through all plant and animal membranes? What is the basis for your answer? What explanation is given for this fact?

CHAPTER XXVI

Fats and Related Substances

FATS

Occurrence. Fats, like carbohydrates, are widely distributed in nature in both plant and animal cells. They are present in the seeds of many plants, and the common names given to them often suggest such origin, as for example, olive oil, peanut oil, cottonseed oil, and corn oil. Fats in seeds function as a stored supply of food, available for plant use as their seeds germinate. Animals store deposits of fat in their adipose tissue cells, which constitutes one provision on the part of nature for storage of a reserve food that can be drawn upon in time of need to supply nutriment for the actively functioning cells (p. 477). Fats, or closely related fat derivatives, are also found within actively functioning cells, being essential components of cell protoplasm.

Synthesis of fats. Fats, like carbohydrates, are composed of the elements carbon, hydrogen, and oxygen. Whether or not *plants* can build their fats directly from carbon dioxide and water is not known; there is, however, good evidence that *plants can make fats from carbohydrates*. For example, it has been observed that, when fats are being made in ripening seeds, as the quantity of fat increases in the seeds there is a corresponding decrease in the quantity of carbohydrate present therein. It has also been noted that sugars are constantly carried in the sap to the cells where fats are being made and that these sugars disappear as the fats appear.

Part of the fat present within fat storage cells of *animals* is provided by fats of the diet, but much of this stored fat is made from glucose. In addition to carefully controlled laboratory experiments which demonstrate this latter origin of stored fat there is also much evidence drawn from common experience; it has long been the practice of farmers to fatten animals by feeding them with corn and grain which are rich in carbohydrates; it is also a matter of common observation that when humans partake freely of sugars and starches, in excess of their carbohydrate needs, they store fat.

Fats and fatty oils. Certain fats, notably those which are liquids as they occur in nature, are commonly referred to as oils, whereas solid fats are simply called fats. But it is well to make note of the fact that this term *oil* is also applied to various substances which are not fats and indeed may bear no chemical relationship to fats.

In general, the term *oil* is applied to any liquid substance or mixture of substances which has a greasy feeling. Thus mineral oil, kerosene oil, and fuel oil are not fats but are rather mixtures of hydrocarbons. The term *oil* is also applied to certain other volatile substances of plant origin which have an oily feeling, as for example, oil of peppermint, oil of wintergreen, and oil of turpentine.

All plant fats are of the liquid variety, such as olive oil, cottonseed oil, and linseed oil; fish fats are also liquid at ordinary temperatures. However, animal fats, other than fish fats, are for the most part semisolid or solid at ordinary temperatures; thus, butter fat and lard are soft solids while beef suet and mutton tallow are harder solids in consistency. But within the *living* animal, fats must be liquid or very soft solids so that muscle mobility will not be impeded. Of course the higher temperature inside than outside the living animal is a helpful factor in this connection; but it is also interesting to note that nature directs that the animal shall make a fat that is adapted to the environment in which it lives or to the kind of skin protection which is natural to the animal. Thus, fish which live in water at a relatively low temperature make liquid fats which have, therefore, a low melting-point. Sheep with their heat-insulating coats of wool make a hard fat with a relatively high melting-point, whereas pigs, which do not provide themselves with such a protection, make a softer fat of a somewhat lower melting-point. The polar bear, although like the sheep it provides itself with a coat of heat-insulating fur, normally lives in a cold climate; as a result it makes a liquid or soft fat which has a low melting-point. Humans make a fat which has a melting-point around 15° C., a fact which may have some bearing on the clothing customs of man in different climates.

Naturally occurring fats. All naturally occurring fats are mixtures. Among the fats commonly found in such mixtures are a hard, solid fat called stearin; a softer, solid fat called palmitin; and two liquid fats called olein and butyrin. The consistency of fat mixtures is, therefore, determined by the proportions of the component fats present therein. Thus, plant fats are liquid because they contain a relatively high proportion of liquid fats, chiefly olein, with solid fats in solution in these liquid fats; butter fat

contains such proportions of the liquid fats butyrin and olein, and the solid fats stearin and palmitin, as give it its familiar soft consistency; human fat is a mixture made up principally of stearin, palmitin, olein, and butyrin in different proportions in different locations in the body.

Physical properties. All fats are greasy. Most fats are colorless, odorless, and tasteless; such tastes and odors as are commonly associated with certain fats are due to the presence of other substances, some of which are made from fats themselves through certain chemical changes which they undergo.

Solubilities and important consequences. Fats are not soluble in water but are soluble in ether, acetone, chloroform, hydrocarbons, in some hydrocarbon derivatives, in other fats, and to a limited extent in hot alcohol.

The water insolubility of fats gives rise to various fat-removal problems which are solved only through a selection of such of these fat solvents as are appropriate for the specific uses. In the "dry cleaning" of clothing various liquid hydrocarbon mixtures are in use, but the fact that these substances burn readily with oxygen at relatively low kindling temperatures makes their use in this connection distinctly dangerous. Carbon tetrachloride, which is an excellent fat solvent, does not react at all with oxygen and is therefore much safer for fat-removal use than are hydrocarbons. In hospital practice ether is sometimes employed in the preparation of the skin for operation, since it produces a more thorough cleansing of the area by dissolving out any oils which may have accumulated in the pores. It should be remembered, however, that prolonged contact of any of these fat solvents with the skin is undesirable because by dissolving and carrying away the natural oils and waxes they leave the skin dry and hard.

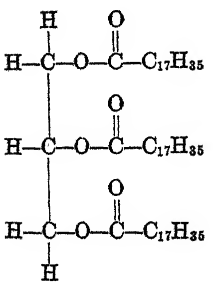
Fats and water when mixed and thoroughly shaken form an emulsion, but such dispersions are only temporary since they show a marked tendency toward separation. However, in the presence of certain substances known as stabilizers or emulsifying agents these dispersions may form more or less permanent emulsions (p. 232). Sodium and potassium soaps, for example, have been found to be good emulsifying agents for keeping fats suspended in water, hence the use of soap and water for the removal of grease from fabrics, utensils, or the skin. Other good emulsifying agents which are used for specific purposes are proteins and gum acacia: mayonnaise, for example, is an emulsion in which egg proteins function as the emulsifying agents; milk is a natural emulsion in which the

proteins present function as the stabilizers for the emulsion; gum acacia is used by the pharmacologist as an emulsifying agent for holding certain oily medications such as cod liver oil in emulsion. From a physiological angle, the emulsification of fats in water facilitates the hydrolysis of fats in digestion by keeping them suspended in small droplets, thereby providing greater surface of contact with the water and with the enzyme steapsin; and among the substances that are always present in the intestinal contents where these reactions take place are bile salts and cholesterol, which are excellent emulsifying agents for fats. In lymph and blood, and in the protoplasm of actively functioning cells the fats are held in fine suspension probably through the emulsifying agency of blood, lymph, and cell proteins which are always present.

Not subject to diffusion. Because fats do not form true solutions with water they are not subject to diffusion through membranes. Hence it is necessary for the fats of the food mass to undergo, first, hydrolysis to make fatty acids and glycerol which can enter the intestinal membrane, then, a remaking before they gain access to the lymph and blood. On the other hand, the very fact that fats cannot pass through a membrane makes them suitable for storage in the cells of both plants and animals; in this way they are able to function importantly as a reserve food which can be drawn upon by the organism in time of need.

Composition. Fats are esters each molecular weight of which is composed of one glyceryl radical and three fatty acid radicals. Some of the fats of common occurrence in natural fat mixtures together with items concerning them are given in the accompanying table (p. 366).

The following semistructural formula which represents one molecule of glyceryl stearate, as a typical fat, indicates the manner in which the glyceryl radical and fatty acid radicals are believed to be combined with each other in all fat molecules:



Note.—Owing to the length of the fatty acid radical carbon chain it is customary to use the semistructural formula for the fat molecule. It is suggested, however, that the student assemble the complete structural formula for the molecule.

Name of the fat	*Formula for the molecular weight and molecule*	*Characteristics of fat*	*Suggestions as to occurrence in natural fat mixtures*
Glyceryl butyrate (Butyrin)	$C_3H_5(C_3H_7COO)_3$	Liquid Saturated	Butter fat, human fat.
Glyceryl palmitate (Palmitin)	$C_3H_5(C_{15}H_{31}COO)_3$	Solid Saturated	Butter fat, lard, tallow, cod liver oil, human fat, cottonseed oil, corn oil, palm oil, peanut oil.
Glyceryl stearate (Stearin)	$C_3H_5(C_{17}H_{35}COO)_3$	Solid Saturated	Butter fat, lard, tallow, cod liver oil, human fat, cottonseed oil, corn oil.
Glyceryl oleate (Olein)	$C_3H_5(C_{17}H_{33}COO)_3$	Liquid Unsaturated	Butter fat, lard, tallow, human fat, cod liver oil, corn oil, olive oil, palm oil.
Glyceryl linoleate (Linolein)	$C_3H_5(C_{17}H_{31}COO)_3$	Liquid Unsaturated	Cottonseed oil, lard, linseed oil, olive oil, peanut oil.

More than one variety of fatty acid radical may contribute to the make-up of the fat. For example, stearo-diolein, which is composed of the glyceryl radical, together with one stearate and two oleate radicals, is said to be present in human fat. Palmito-distearin is present in both lard and beef fat. Such fats are known as mixed fats, in contrast with fat mixtures.

In general, the fatty acid radicals which contribute to the make-up of fats are of high radical weights, hence the fats themselves are compounds of high molecular weight, stearin being one of the heaviest of the fats while butyrin is the lightest. It is also interesting to learn that practically all *naturally occurring fats contain only fatty acid radicals which have an even number of atomic weights of carbon in their molecular weights,*[1] the butyrate having *four*, the palmitate having *sixteen*, and both the stearate and oleate having *eighteen* atomic weights of carbon in their radical weights. Probably this is not without biological significance, as we shall see later when the oxidation of fats in the cells and the manner of their making are presented.

[1] An unsaturated fatty acid having the formula C_4H_7COOH has been found in croton oil: and iso-valeric acid, having the formula C_4H_9COOH, has been isolated from the blubber of porpoises. Bodansky, Meyer, *Introduction to Physiological Chemistry*, John Wiley and Sons, 1938, p. 66.

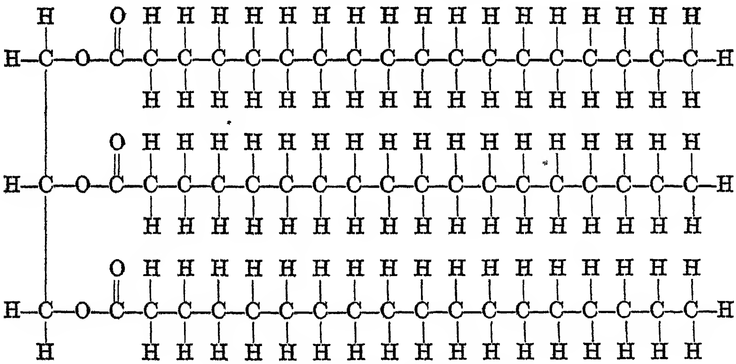
Although fats, like carbohydrates, are composed only of the elements carbon, hydrogen, and oxygen, it will be observed from their formulas that fats have relatively much less oxygen in their make-up than do carbohydrates.

Saturated and unsaturated fats. Some fats, glyceryl stearate, glyceryl palmitate, and glyceryl butyrate among them, are saturated fats, whereas others, including glyceryl oleate and glyceryl linoleate, are unsaturated fats. An *unsaturated fat* is a fat the acid radical of which is capable of entering into direct combination with hydrogen and with certain other substances to make saturated compounds. For example, glyceryl oleate, a typical unsaturated fat, reacts with hydrogen, in the presence of a suitable catalyst, to make glyceryl stearate which is saturated:

$$C_3H_5(C_{17}H_{33}COO)_3 + 3\ H_2 \longrightarrow C_3H_5(C_{17}H_{35}COO)_3$$

Saturated fats cannot react in direct combination with other substances.

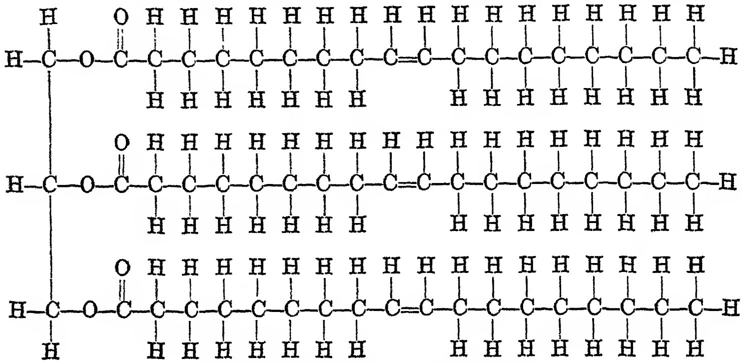
Theoretically, the difference in this chemical behavior as to saturated and unsaturated fats lies in the make-up of the molecule. In a *saturated fat* molecule all of the carbon atoms in the fatty acid radicals are believed to be combined with each other by *single* bonds, a condition which is represented in the following structural formula for the molecule of glyceryl stearate:



Glyceryl stearate, a saturated fat

But in the molecule of an *unsaturated fat* one or more pairs of carbon atoms in the fatty acid radical or radicals are supposed to be combined with *double* bonds. It is at these points in the molecule, then, that the addition of hydrogen or other atoms may take place to make a saturated compound. This unsaturated condition is illustrated by the following structural formula for the glyceryl

oleate molecule in which a double bond is believed to be present between the ninth and tenth carbon atoms in the fatty acid radicals:



Glyceryl oleate, an unsaturated fat.

Glyceryl linoleate is an even more unsaturated fat than is glyceryl oleate, in that, supposedly two pairs of carbon atoms are joined by double bonds in the carbon chain of the lineoleate fatty acid radicals.

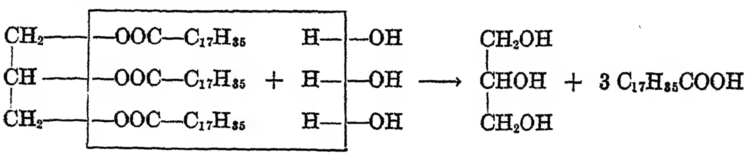
Saturated fats and unsaturated fats show characteristic differences both as to physical state and chemical behavior. Unsaturated fats are liquid while most saturated fats are solid. Unsaturated fats make addition products and are generally more active chemically than are saturated fats. This greater activity of unsaturated fats is probably of significance physiologically, since it has been discovered experimentally that a desaturization of fatty acid radicals is constantly going on in the liver, perhaps preparatory to the distribution of more active fats to actively functioning cells (p. 475).

Chemical behavior. ***Hydrolysis.*** All fats react with water in double decomposition to make fatty acids and glycerol, as in the reaction represented by the following equations:

For either the mass or molecule reaction, formulas given empirically.

$$\text{Glyceryl stearate} + \text{Water} \longrightarrow \text{Glycerol} + \text{Stearic acid}$$
$$C_3H_5(C_{17}H_{35}COO)_3 + 3\,HOH \longrightarrow C_3H_5(OH)_3 + 3\,C_{17}H_{35}COOH$$

For molecule reaction.



Hydrolysis of fats can be speeded up to appreciable proportions by exposure to very high temperatures, as in reaction with superheated steam; or at the lower temperature of long boiling in the presence of a dilute acid or base, perhaps acting as a catalyst; or at ordinary temperatures through the agency of enzyme catalysts which are called lipases and which are made in certain plant and animal cells.

The wide distribution of lipases in both plant and animal cells would indicate that fat hydrolysis reactions are of considerable biological importance. In the human body the digestion of fats involves their hydrolysis favored by catalysts of this type. Fats which are already in natural emulsification, such as milk fat and butter, are subject to gastric hydrolysis, a gastric lipase made in the glands of the stomach acting as a catalyst; steapsin, a lipase made in the pancreas and delivered into the duodenum, favors the hydrolysis of all fats in the intestine. Lipases are also found in the cells; and it is believed that hydrolysis of fats to fatty acids and glycerol is the first step in fat oxidation. (For further discussion see pp. 472 and 473.)

With bases to make soaps. Fats react with sodium and potassium hydroxides to make soaps and glycerol. For example:

$$\underset{C_3H_5(C_{17}H_{31}COO)_3}{\text{Glyceryl stearate}} + \underset{3\,NaOH}{\text{Sodium hydroxide}} \longrightarrow \underset{C_3H_5(OH)_3}{\text{Glycerol}} + \underset{\substack{3\,C_{17}H_{31}COONa \\ \text{(a soap)}}}{\text{Sodium stearate}}$$

Such reactions are of great commercial importance in the soap industry. Although various processes for the making of soap are in use, the principle involved is the same. The fat and sodium hydroxide solution are kept in contact for some time at a high temperature to speed up the reaction. The soap is then separated from the glycerol by "salting it out," that is, sodium chloride is added in a sufficient quantity to result in a solution of greater density than that of the soap, in which event the soap automatically rises to the top of the mixture. When the soap has been removed the glycerol is separated from the salt solution and is a valuable by-product of the soap industry. Sodium soaps are hard soaps, potassium soaps are soft.

Actually this reaction probably takes place in two stages, first the hydrolysis of the fat, the base acting as a catalyst:

$$C_3H_5(C_{17}H_{35}COO)_3 + 3\,HOH \xrightarrow{\text{Sodium hydroxide}} 3\,C_{17}H_{35}COOH + C_3H_5(OH)_3$$

then a second reaction between the fatty acid and the base to make the soap and water:

$$C_{17}H_{35}COOH + NaOH \rightarrow C_{17}H_{35}COONa + H_2O$$

Hydrogenation of unsaturated fats. The fact has already been mentioned that hydrogen can be made to combine with unsaturated fats to make saturated fats. Such reactions are very slow unless favored by a catalyst, and nickel is one catalyst which has been found to function satisfactorily in this connection (p. 65). Within recent years fat hydrogenation has developed into a business of considerable importance as a means for making solid fats from liquid fats, solid fats being the more desirable fats both for foods and for making soap. Vegetable fats which are used for this purpose, such as cottonseed oil, corn oil, peanut oil, etc., contain a high proportion of the liquid fat, olein, from which, by hydrogenation, stearin, a solid fat, is made. Hydrogenation of the liquid fat is continued until the proportion of olein to stearin is such as to provide a fat mixture of the desired consistency:

$$\underset{\text{Olein, a liquid fat}}{C_3H_5(C_{17}H_{33}COO)_3} + 3\ H_2 \xrightarrow{\text{Nickel}} \underset{\text{Stearin, a solid fat}}{C_3H_5(C_{17}H_{35}COO)_3}$$

Stearin thus obtained, being of the same composition as animal stearin, has exactly the same nutritional value as that made by nature. Lard substitutes made from vegetable fats after this manner have become an invaluable supplement to the world's supply of natural solid fats, since the latter are not made by nature in animals in sufficient quantities to meet all needs.

Auto-oxidation of unsaturated fats. As has previously been stated unsaturated fats are more active chemically than are saturated fats. They are capable of entering into combination with oxygen slowly to make saturated compounds even at ordinary temperature and without the presence of a favoring catalyst. Such reactions are called auto-oxidation. Reactions of this sort are in part responsible for the tendency of liquid fats to become rancid.*

* The term *rancid,* applied to fats and fatty oils, refers to certain changes which result in compounds that have either an undesirable taste, or odor, or both. In general two types of chemical reactions may be involved: hydrolysis reactions (as in the case of butter in which the butyric acid produced is largely responsible for the taste and odor effects) or the oxidation of unsaturated fats. The two types of chemical change are often associated.

This type of reaction is also involved in the *"drying" of paint;* paint pigments are mixed with linseed oil which has as components

several unsaturated fats, and these fats upon reacting with oxygen make saturated compounds which are solids; the turpentine of frequent use with paints acts as a catalyst to speed up this reaction with oxygen. *Physiologically*, it is believed that auto-oxidation reactions on the part of unsaturated fats, or fatty acids, are of great importance among the reactions going on in active tissue cells.

SUBSTANCES RELATED TO FATS

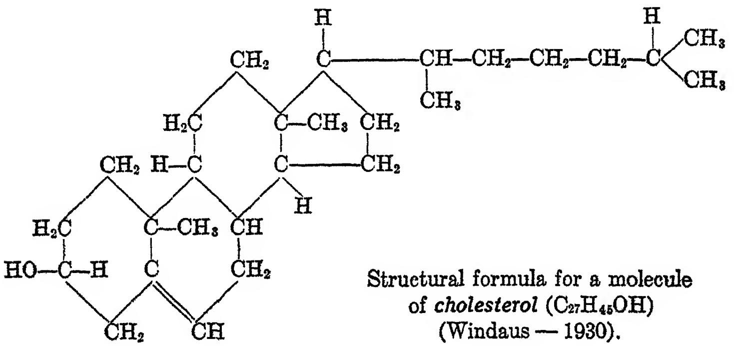
Sterols. Chemically, sterols are alcohols of high molecular weight. They are solids at ordinary temperature, hence the origin of their class name, sterol, which literally means solid alcohol. Sterols are widely distributed in nature, often in association with fats. They resemble fats in their physical properties, being greasy as to feeling, not soluble in water but somewhat soluble in fat solvents. Three of the known sterols which are of especial physiological importance are cholesterol, whose empirical formula is $C_{27}H_{45}OH$, ergosterol represented by the formula $C_{28}H_{43}OH$, and calciferol or vitamin D_2, an isomer of ergosterol.

Cholesterol and its physiological and pathological importance. Cholesterol, the most important sterol, was first isolated from gallstones. It is now known to be present in all living animal cells, but it is especially abundant in nerve tissue where it contributes to the myelin sheath and to a lesser extent to the gray matter. It is believed to be an essential component of protoplasm where it functions, in one respect, and in association with the phospholipids (p. 373), to give the cells the power of holding large quantities of water while still retaining their semifluid consistency. It is believed to be one of the substances responsible for maintaining normal conditions in relation to the permeability of cell membranes. Cholesterol also checks the activity of lipases and in this way probably helps to control the hydrolysis of fats within the cells. It combines with certain hemolytic substances, notably bile salts; and since bile salts are always present in the blood it may be that the cholesterol there present provides one of the control agents for preventing the hemolysis of red blood cells. It probably contributes to the synthesis of bile salts since it bears a close chemical relationship to these compounds.

Cholesterol is also of interest from a pathological angle. It is present in more than normal amounts in the cerebrospinal fluid of the syphilitic and may be one of the substances involved in the Wassermann reaction. It is a substance which is difficult to keep

in solution, being insoluble in dilute acid and dilute base solutions; consequently, if there is a higher than normal concentration of cholesterol in the blood, lymph, or cells there is a possibility that some of it may be precipitated. In fact, deposits of cholesterol are sometimes found along the walls of the arteries in arteriosclerosis, and in the kidneys in nephritis. Cholesterol also plays an important part in the formation of gallstones, some gallstones having been found to contain as high as 98 per cent cholesterol.

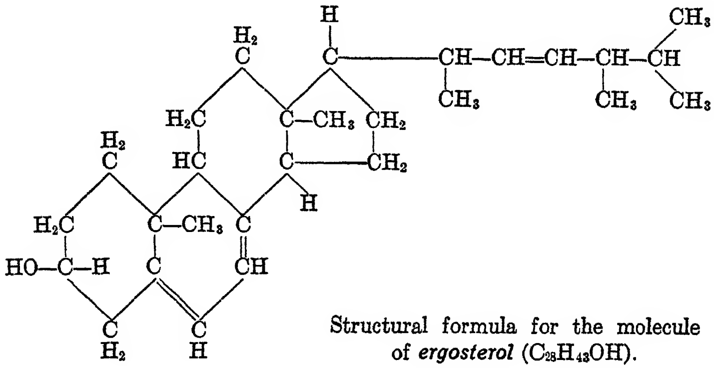
There is good evidence that cholesterol can be synthesized within animal cells. The structural formula for this important compound is claimed to be as follows:



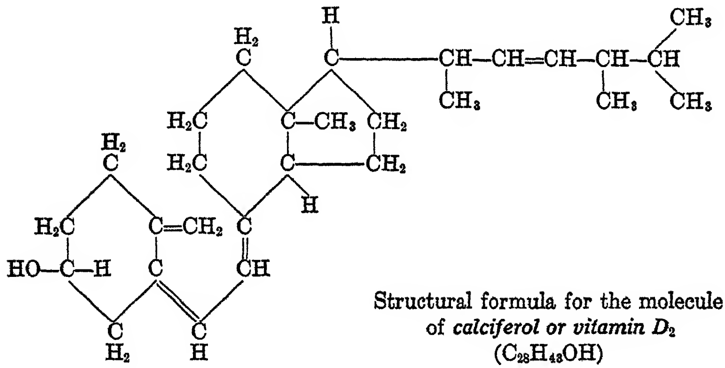
Structural formula for a molecule of *cholesterol* ($C_{27}H_{45}OH$) (Windaus — 1930).

***Ergosterol and calciferol or vitamin D*$_2$.** Ergosterol is a sterol which occurs in both plant and animal cells. It was first discovered in ergot and is very abundant in yeast. Ergosterol is of special interest because it is the precursor of calciferol or vitamin D_2 which has antirachitic properties. When ergosterol is irradiated with ultra-violet rays, either artificial or of the sunlight, calciferol is made. Unfortunately, however, reaction does not stop at this stage, but on continued exposure to ultra-violet rays other substances are produced one of which has been named toxisterol because of its marked toxicity. Within recent years it has been discovered that ergosterol is present in skin cells, hence, on exposure to sunlight, the body can make vitamin D_2 from this source. This helps to explain a fact that has long been recognized: namely, that rickets is more common among children living in dark quarters than among children who are exposed to sunlight out-of-doors. But at the other extreme, an undue exposure to sunlight treatment may lead to the making of some toxisterol.

The following structural formulas for the molecules of ergosterol and calciferol indicate their marked chemical similarity:



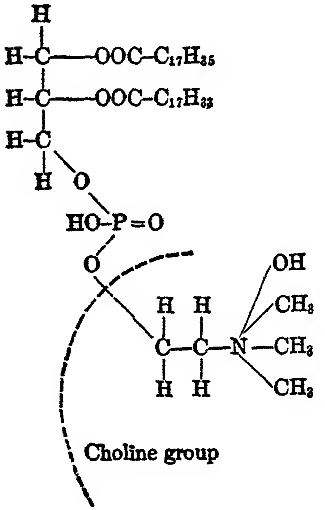
Structural formula for the molecule of *ergosterol* ($C_{28}H_{43}OH$).



Structural formula for the molecule of *calciferol or vitamin D_2* ($C_{28}H_{43}OH$)

Phospholipids and their physiological importance. Phospholipids are compounds chemically related to the fats and resembling them in solubilities. They are present in all plant and animal cells, and are especially abundant in the cells of the brain, liver, muscles, bone marrow, heart, and kidneys, also in eggs. Physiologically they are probably of even greater importance than are fats. Phospholipids are more complex in their chemical make-up than are fats, and less well understood by the chemist. Experimental evidence supports the belief that the molecule of a typical phospholipid contains a glyceryl radical (usually), fatty acid radicals (usually one being of the unsaturated variety), and a phosphoric acid radical which is, in turn, combined with a nitrogen-containing complex. It will be seen that even within these limitations many different phospholipids are possible. One of the best known mem-

bers of the group is a lecithin found in egg yolk. The following formula has been assigned to this compound:



The suggested composition of the molecule of a lecithin, one of the *phospholipids.*

Phospholipids are believed to be essential components of the protoplasm of all animal cells. In association with cholesterol they are probably responsible for maintaining the semifluid consistency of protoplasm. They provide a medium in which fat-soluble and water-soluble substances can be brought into intimate contact with each other. They probably take part in the absorption of fatty acids and in their transportation in the blood and lymph.

Waxes. Waxes are related to fats: chemically, they are esters which contain fatty acid radicals, but the hydrocarbon radical is obtained from a long chain alcohol instead of from glycerol; physically, they have solubilities similar to those of fats. One component of beeswax is the ester myricyl palmitate, a wax which is represented by the following formula:

$$\underset{\text{Palmitate radical}}{C_{15}H_{31}COO}\text{———}\underset{\text{Myricyl radical}}{C_{30}H_{61}}$$

Both plant and animal cells secrete waxes. Bees, of course, are responsible for beeswax; and sheep secrete a mixture of waxes, commonly known as lanolin, which is composed of the stearate, oleate, and palmitate esters of cholesterol. Sebaceous glands of the skin of humans also secrete a wax, another ester of cholesterol, which serves to keep the epidermis of the skin soft; and, because

of the insolubility of this skin wax in water, as well as in dilute solutions of acids, bases, or salts, it is not easily removed. The major components of the cerumen, which is secreted by the ceruminous glands of the external ear, are also waxes.

Questions

1. Compile a list of ten commonly occurring fat *mixtures*, classifying them as to plant or animal origin. Indicate in the case of each fat its characteristic physical state. In general what appears to be the physical state characteristic of plant fats? Of most animal fats?

2. From what substances are fats believed to be synthesized (a) in plant cells, (b) in animal cells? Concerning (a) and (b) what experimental evidence gives reason for the belief in each instance?

3. Make a general statement as to the solubilities of fats. Compare the following agents as to their suitability for the removal of grease spots considering — efficiency, safety, and economy: carbon tetrachloride, chloroform, ether, ethyl alcohol, gasoline, and water.

4. Why is it desirable to protect the hands from contact with the agents commonly used for "dry cleaning" in the home? (What agents?)

5. What is the purpose of the ether wash sometimes used in preoperative preparation of the skin?

6. List at least five *individual* fats, giving names, empirical formulas, and semistructural formulas. For one of the selected fats assemble the complete structural formula for its molecule.

7. a. What is the difference (factual) between a saturated and an unsaturated fat?
   b. How, theoretically, is this difference accounted for?
   c. Give examples of at least one fat of each variety — with name and formula for each.

8. Why should fats be expected to be subject to hydrolysis? Do such reactions take place readily? Give reason. What, in general, are the products of the hydrolysis of fats? Name two specific enzymes of this character. What is the class name given to enzymes which favor such hydrolysis? Assemble word and formula equations for the hydrolysis of five fats.

9. What reaction can be expected from the contact of fats with sodium or potassium hydroxide? Assemble word and formula equations for a typical reaction of this variety.

10. What is the nature of the reaction involved in the hydrogenation of fats? Why are such reactions of commercial importance? Assemble word and formula equations for the hydrogenation of olein.

11. Linseed oil is frequently used in paint mixtures. What is the nature of the change involved in the drying of such paints?

12. What is a sterol? Name two which are physiologically important, stating their occurrence and the physiological functioning of each.

13. What is a phospholipid? Where do such compounds occur? Name at least one respect in which they are important physiologically.

14. What is the chemical nature of a wax? Name some common waxes or mixtures with wax components, stating their occurrence.

CHAPTER XXVII

Cyclic Compounds and Derivatives

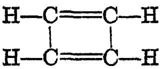
Importance. Organic compounds which have so far claimed our attention have been in the main of the straight carbon chain variety. And the fact is that most organic compounds of biological importance are members of this group. However, before we can make an intelligent study of proteins, and of many other compounds of considerable importance in the concerns of man, it is desirable to become better acquainted with the second great class of organic compounds known as *aromatic* or *cyclic* compounds. Certain of the amino acids which contribute to the make-up of proteins are derivatives of these cyclic compounds as are also various other substances of physiological importance, as for example, the sterols previously mentioned (p. 371), and the hormones thyroxine (p. 481) and epinephrine (p. 481). Many drugs and disinfectants are cyclic derivatives and their number is increasing year by year as pharmaceutical chemists experiment in their laboratories making new drugs or modifying old ones, ever hoping to obtain compounds more effective, more nearly free from undesirable side actions, or in other ways better suited to the physician's use. Dyes adapted to a variety of uses have been made as derivatives of cyclic compounds — dyes for bacteriological stains (p. 392), for disinfection (p. 395), for diagnostic tests (p. 397), and for testing for hydrogen ion and hydroxyl ion concentrations. And the great increase within recent years in the number of new dyes for coloring purposes has resulted from the development of the chemistry of cyclic compounds; not only is there a much greater variety of shades than was available in the days of our grandmothers, but there are more dyes of lasting colors (less subject to fading), and more acid fast and base fast dyes than formerly. In fact the development of the dye industry, along with the development of the chemistry of the cyclic compounds, is a story in itself. Nor must we leave this listing of cyclic derivatives without including flavors, perfumes, modern photographic supplies, explosives, synthetic resins, and plastics. Indeed, an attempt to enumerate the many compounds of cyclic origin which are of importance and

in common daily usage in these modern times would be an impractical task, since more than half of the many thousands of known organic compounds are of cyclic derivation.

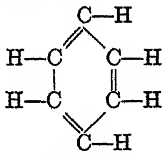
Significance of class names. The class name, ***aromatic***, came to be applied to these compounds because many, though by no means all, of them have fragrant odors as of fruits, spices, and balsams. Some have less pleasant odors: the odor of feces, for example, is due to the presence of certain compounds (p. 402) of the cyclic variety. However, this property of odor is not distinctive of cyclic compounds; substances other than cyclics have odors and many of the cyclic compounds are odorless. Consequently, this class name of aromatics cannot be regarded as of any great significance. The other class name, ***cyclics***, has a decided chemical bearing. It signifies the belief of the chemist that within molecules of all members of this family of compounds are to be found carbon atoms, and frequently other atoms, combined with one another in a *closed chain or ring formation.*

Carbocyclic and heterocyclic compounds. If there are only carbon atoms in this closed ring structure the compound is referred to as a *carbocyclic;* if an atom or atoms of some other element are included in the ring the compound is classed as a *heterocyclic.* The following are structural formulas for some of these cyclic compounds:

Carbocyclic compounds

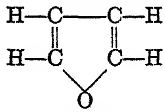


Cyclo butene

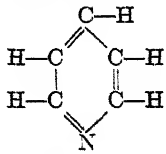


Cyclo hexene
or
Benzene

Heterocyclic compounds



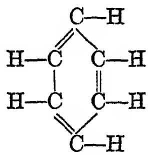
Furan



Pyridine

Reasoning which leads to the belief in cyclic structures. Benzene is one of the simplest of the cyclic compounds, also it is the aromatic compound which has more derivatives than any other cyclic. But for years after it became *known* that its molecular weight is composed of six atomic weights of carbon and six atomic weights of hydrogen, chemists were puzzled as to how the *presumable* six atoms of carbon and only six atoms of hydrogen could be arranged within a molecule and still provide for a four valence for each carbon atom and a one valence for each hydrogen atom.

Alternate single and double valence bonds. It was in 1865 that the chemist Kekulé suggested that possibly *the carbon atoms are combined in a ring formation with alternate double and single valence bonds,* the fourth bond on each carbon atom being satisfied by the one valence bond of a hydrogen atom. These conditions are represented in the following structural formula:

Benzene	*Empirical formula for molecular weight and molecule.*	*Structural formula for molecule*
	C_6H_6	

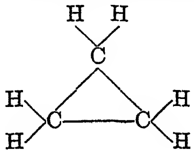
A study of this structural formula for benzene indicates that, with such an arrangement, each of the six carbon-hydrogen atom groups should have exactly the same relationship in respect to the rest of the molecule and be susceptible to the same chemical attack; and there are factual findings which support this belief. Simple as these suggestions made by Kekulé may seem to the student of today, they formed an epoch in the history of chemistry and led to a fairly satisfactory explanation as to the composition of many organic compounds, other than benzene.

One cause for dissatisfaction with this molecule set-up is in respect to the double bonds in the ring structure. Their presence suggests an ability on the part of the carbon atoms to reach out to make addition products with other atoms, whereas the actual fact is that although benzene and other cyclic compounds can enter into direct combination with other substances, they do so with difficulty. So the student must remember that, when atoms are joined with a double bond in ring formation, the same chemical activity significance is not implied as is the case when carbon atoms are joined by double bonds in the straight chain hydrocarbons (p. 294).

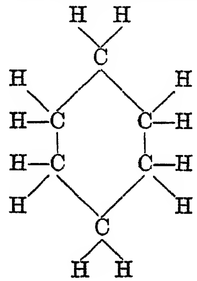
Cycloparaffins or single valence bond formation. But there are also compounds whose chemical composition and chemical behavior can best be explained by the assumption that certain carbon atoms within their molecules, although combined within ring formation, are joined *only with single valence bonds.* One such is the gaseous hydrocarbon cyclopropane which has come into prominence as an anesthetic; its molecular weight has a known empirical formula of C_3H_6, its molecule has a believed-in structural formula as given below. Another such compound is cyclohexane whose molecular

weight has a known empirical formula of C_6H_{12}. These two compounds, cyclopropane and cyclohexane, are isomeric with the straight chain hydrocarbons, propene and hexene, but there is this important difference: chemically, cyclopropane and cyclohexane are saturated whereas propene and hexene are unsaturated. The accepted structural formulas for molecules of these two typical cyclic saturated hydrocarbons are as follows:

Cyclopropane (C_3H_6)

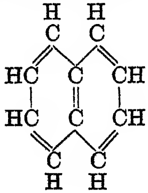


Cyclohexane (C_6H_{12})

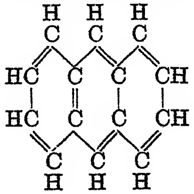


Condensed cyclics. There are still other organic compounds whose known composition has led to the supposition that within their molecules there are *two or more cyclic structures in combination with each other.* For example, the molecular weight of the hydrocarbon naphthalene has a known composition, as represented in the empirical formula $C_{10}H_8$, which is accounted for by such an atom placement within its molecule as is represented in the accompanying structural formula. Similarly, the composition of the isomeric hydrocarbons anthracene and phenanthrene, with a known composition as represented in the formula $C_{14}H_{10}$, are explained through the belief that within their molecules the placements of the atoms concerned are as represented in the following structural formulas. Compounds such as naphthalene, anthracene, and phenanthrene, whose molecules are supposed to contain two or more carbon rings in combination with each other, are known as *condensed cyclics.*

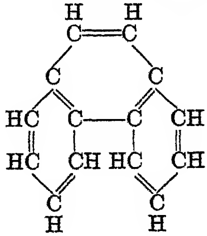
Naphthalene ($C_{10}H_8$)



Anthracene ($C_{14}H_{10}$)

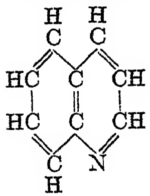


Phenanthrene ($C_{14}H_{10}$)

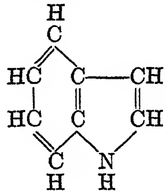


The composition of some *heterocyclic* compounds is also explained through the assumption of similar cyclic condensations within their molecules. Two such compounds are quinoline (C_9H_7N) and indole (C_8H_7N) whose accepted structural formulas for their respective molecules are as given below:

Quinoline (C_9H_7N)



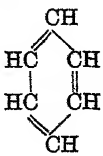
Indole (C_8H_7N)



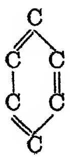
Various methods for representing cyclic structural formulas. The six carbon atom ring that is characteristic of the benzene molecule, whether present all by itself or as a nuclear part of molecules of benzene derivatives, is known as the *benzene ring.* It is represented on the printed page in various abbreviated forms, and because of the frequency with which these abbreviations are encountered in the literature, it is well for the student to become acquainted with them.

The complete structural formula for benzene is given under A. But sometimes only the carbon atoms in the ring and the valence bonds are represented (as in B), in which case it is understood that only hydrogen atoms are present in the positions necessary to satisfy the fourth valence of each carbon atom. When both carbon and hydrogen atoms are omitted (as in C), the reader must then understand that their presence in the usual positions is taken for granted. Still another form of abbreviation is to use heavy lines to represent positions of double bonds and lighter lines to represent positions of single bonds (as in D):

A



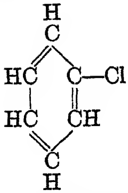
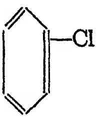
B



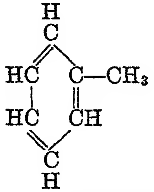
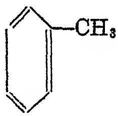
C

D

Substituted atoms or atom groups that are peculiar to the specific benzene derivative are always represented. Thus the complete structural formula for monochlorobenzene and methyl benzene are given below in E and G. But frequently these formulas appear in abbreviated manner as in F and H, in which case it is understood that carbon atoms are combined in the ring structure while the fourth valence bond for each carbon atom is satisfied by a hydrogen atom, save at the point where the specified substituent is located:

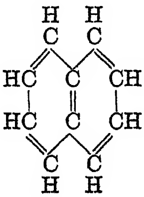
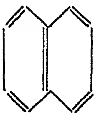
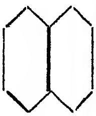
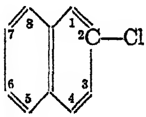
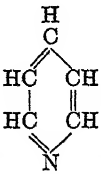
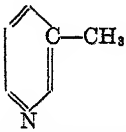
E  F 

Monochlorobenzene

G  H 

Methyl benzene

The same type of abbreviation is used for the structural formulas of other cyclic compounds and their derivatives. Thus:

The compound with its empirical formula	*Complete structural formula*	*Two types of abbreviated formulas*	*A derivative, with name*
Naphthalene $C_{10}H_8$		 	 2-monochlornaphthalene. Carbon atom positions are numbered to indicate the location of the derivative.
Pyridine C_5H_5N		 	 3-methyl pyridine

Occurrence. The aromatic or cyclic compounds occur in nature in great numbers and varieties within the cells of plants but to a much less extent within animal cells. It would appear that whereas plants can synthesize these ring compounds from carbon dioxide and water, drawing upon nitrates and other compounds as needed, animals lack this power, hence they must obtain from plants of their food supply the parent compounds from which to build such cyclic derivatives as they require. More will be said later with regard to this dependence of animals upon plants. Herein, too, lies the explanation for the fact that for centuries man has turned to

plants for certain drugs, poisons, perfumes, flavors, and dyes, since these substances contain cyclic structures that only plants can make. And we are told further that each plant makes such cyclics and cyclic derivatives as are peculiar to its own needs: thus, the opium poppy makes the cyclic complex peculiar to morphine (p. 406); the checkerberry makes the cyclic derivative peculiar to wintergreen (p. 400); peas and beans make the cyclic indole (p. 402) which is an essential constituent to one of the amino acids which, in turn, contributes to the proteins of these plants; and the madder makes the cyclic derivative peculiar to it, which by our forebears was named turkey red because of its color. Some of these compounds — morphine, for example — the chemist has never learned to duplicate in the laboratory; other cyclic derivatives found in nature — the flavor component of wintergreen and the dye turkey red, for example — are being synthesized in large quantities. However, chemists have been interested not only in duplicating such compounds as are found in nature but also in making new and different cyclic derivatives, and thousands such have been made.

Components of coal tar. An important commercial source of parent ring structures for synthetic cyclic derivatives is soft coal, the desired compounds becoming greatly concentrated in the coal tar mixture as coal is destructively distilled. In this way compounds once made in the cells of living plants, buried centuries ago in the crust of the earth as the result of some great earth upheaval, are again rendered available for the use of man in making numerous useful substances.

Coal is a mixture of very complex compounds which, when heated to a high temperature in a closed container, decompose to make simpler compounds. Such decomposition, through the agency of heat and out of contact with air, is called *destructive distillation.* For many years coal was submitted to this process either for the sake of the hydrocarbons of illuminating gas or for the coke obtained, the coal tar by-product being regarded as a necessary nuisance and utter waste, save for the relatively small quantities used for such purposes as making tar paper and surfacing roads. Even today this is the fate of much of the coal tar thus produced. It was an important day in industrial history when the chemist began to consider the possible treasure hidden away in this ill-smelling, black, sticky mass. The details of the destructive distillation of coal process and a listing of the numerous compounds obtained therefrom can be obtained from many sources. For our purposes the following simple experiment will give more meaning to this subject.

The apparatus set-up for this experiment is suggested by the accompanying diagram. The pyrex test tube is partially filled with soft coal. The first bottle is for the collection of the coal tar mixture; the second bottle contains

water for the collection of soluble gases — note that the entering delivery tube reaches down into the water so that the gases must pass up through the same; a third bottle, containing water, is inverted in a cistern of water and is for collection, by water displacement, of insoluble gases.

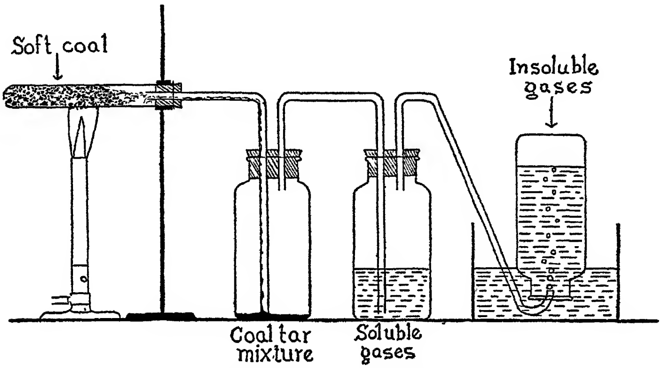
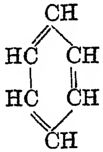
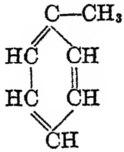
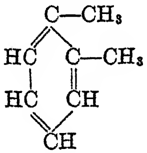
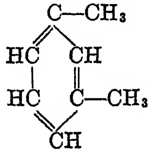
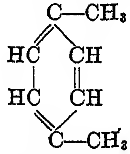
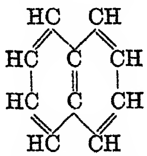
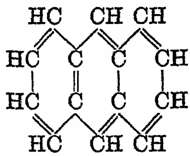
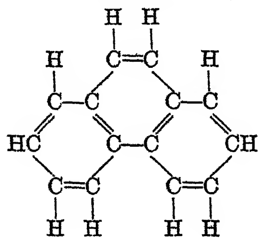


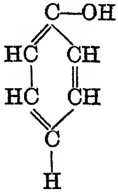
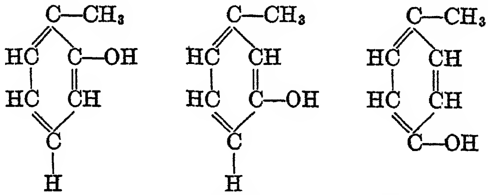
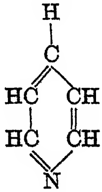
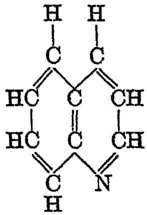
FIG. 89. The Destructive Distillation of Coal

When the apparatus is set up in good order and all connections are airtight, the test tube containing the soft coal is heated gently at first, then with full flame. Continuous heating is necessary with the burner adjusted to provide the maximum heat of which it is capable. Presently, a heavy, brownish yellow vapor appears in the tube and condenses in the first bottle into a thick, sticky, brown mixture of liquid and solid substances called coal tar. Indeed, it seems incredible that this crude-smelling, unpleasant-looking mass could possibly contain substances from which perfumes with delightful odors and dyes with pleasing colors can be made. The less dense, gaseous substances continue on to be collected in the second and third bottles. Ammonia is the most important of the soluble gases collected and it reacts with water to make ammonium hydroxide ($NH_3 + H_2O \longrightarrow NH_4OH$). The insoluble gases collected by water displacement are chiefly the hydrocarbons of illuminating gas mixture. The student can verify the claim that these hydrocarbons burn by removing from the cistern the bottle either partially or completely full of the gas and bringing a lighted match to its mouth. When the heating of the soft coal has been continued until all of the complex compounds of the coal which are subject to destructive distillation have been decomposed, the remaining black material left in the test tube is chiefly coke.

A few of the most important compounds that are present in coal tar mixture and which are separated therefrom for use as parent structures for the making of other compounds are listed on pages 384–385. From these compounds, and from others not presented, literally thousands of derivatives have been made and undoubtedly thousands more are possible.

Name	*Structural formula for molecule*	
Benzene [1]		From which are derived many drugs, disinfectants, dyes, etc.
Toluene [1] (Methyl benzene)		Parent substance for flavors, perfumes, dyes, and explosives. The famous T.N.T. (trinitrotoluene) is a derivative.
Three xylenes [1] (Dimethyl benzene)	  	From which are derived perfumes, dyes, explosives, etc.
Naphthalene		Commonly met with in moth balls. An important parent substance for disinfectants, dyes, flavors, and perfumes.
Anthracene		Parent substance for many dyes: for example, alizarin, commonly known as "turkey red."
Phenanthrene		Morphine, codeine, and heroin are derivatives of phenanthrene. However they are still obtained directly from the opium poppy with the exception of heroin, which is a synthetic compound.

[1] Benzene, toluene, and xylene are sold commercially as benzol, toluol, and xylol respectively. This is unfortunate since the ending *ol* indicates an alcohol and none of these compounds is an alcohol. Xylene (labeled xylol) is commonly used in the laboratory as a solvent for cleaning the oil immersion lens of the microscope.

Phenol (Carbolic acid)		Various drugs, disinfectants, dyes, and explosives are derived from phenol.
Three cresols		Antiseptics and disinfectants. Components of lysol and tricresol.
Pyridine		A heterocyclic compound from which various drugs are derived. It is a constituent of nicotine, although this drug is obtained from tobacco leaves rather than from coal tar.
Quinoline		Plasmochin, a synthetic compound used for the treatment of malaria, is a quinoline derivative. Quinine, although obtained from the bark of the cinchona tree rather than from coal tar, is also a quinoline derivative.

Regarding chemical behavior. It is not our purpose, nor indeed would it be advisable within the limits of this text, to discuss in detail the chemical behavior to be expected on the part of this large family of organic compounds. But a few points which it would be well to keep in mind in this connection are as follows. *First:* the ring structure itself is very stable. It does not tend to break when the molecule becomes involved in reactions, but rather appears as a unit part of the new molecule that results from the reaction. Indeed, it is only with difficulty that reactions can be brought about which will cause a break in this ring formation. *Second:* cyclic compounds show little tendency to enter into

chemical reactions to make addition products on the ring, although such "additions" can be effected with difficulty on atoms in the ring which are joined with double bonds; and when this does happen, the double bonds affected give way as usual to single bonds. *Third:* cyclic structures do enter into reactions with greater or less ease to make substitution products on the ring, a fact which makes possible the synthesis of a great variety of derivatives. *Fourth:* the chemical behavior of cyclic derivatives is determined in part by the behavior of the cyclic portion and in part by the behavior of the atom group or groups which are present as side chains attached to the ring, each participating in reactions characteristic of it. Some of these reactions will be considered presently under the more detailed study of carbocyclics.

CARBOCYCLICS

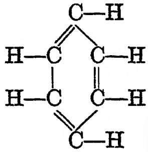
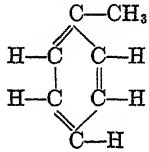
Benzene and toluene. Benzene, as has been said previously, is one of the most important of the cyclic compounds because of the great number of useful derivatives that are made from it. Perhaps next in importance comes toluene, but toluene is really a derivative of benzene; it is methyl benzene in fact, although it is not necessary to turn to benzene for its making, since plenty is found already made in the coal tar mixture.

Benzene is a colorless, volatile liquid and is an excellent solvent for other hydrocarbons, for fats, paints, varnishes, resins, and many other compounds. It is used extensively in a great variety of industries, including dry cleaning and the manufacture of synthetic rubber, munitions, dyes, paints, and leather substitutes.

Physiological effects. Exposure to only small amounts of benzene over a long period of time results in a destructive attack upon red blood cells and platelets. The breathing of concentrated benzene vapor results in central nervous system depression, and death may follow due to respiratory failure. Because of these physiological effects, benzene constitutes a hazard for workers in the many industries in which it is used.

Toluene is frequently used in hospital practice as a preservative for urine specimens. This may not be due to any disinfectant action on the part of toluene but rather to its being immiscible with, and lighter than, water, which properties cause it to form a protective layer on the top of the specimen, thereby excluding contamination from the outside. Toluene is chiefly important as a parent substance for the making of very useful compounds.

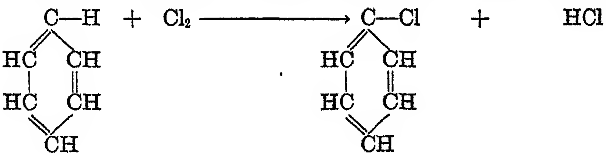
Some outstanding derivatives of both benzene and toluene will be given presently.

Benzene		*Toluene or Methyl benzene*	
Empirical formula for molecular weight and molecule	Structural formula for molecule	Empirical formula for molecular weight and molecule	Structural formula for molecule
C_6H_6		C_7H_8	

Chemical behavior of cyclic hydrocarbons and naming of derivatives. Since benzene is entirely a *carbocyclic*, a study of chemical reactions in which it will participate will point the way to what can be expected in the way of chemical reactions from all carbocyclic compounds.

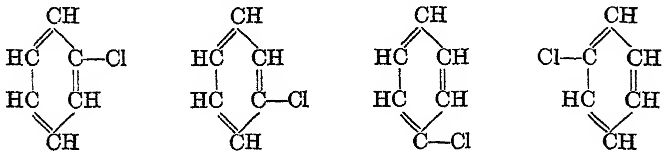
With chlorine and bromine benzene will react under appropriate conditions to make hydrochloric acid and chlorobenzene derivatives, or hydrobromic acid and bromobenzene derivatives. The simplest of these derivatives with chlorine is monochlorobenzene and the following equation represents the molecule involvement in the reaction:

Benzene + Chlorine ⟶ Monochlorobenzene + Hydrochloric acid



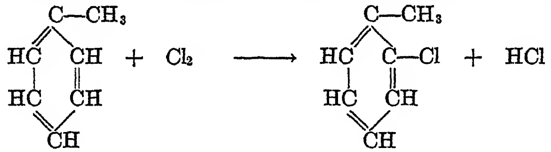
Since all of the carbon-hydrogen atom groups bear the same relationship to the benzene molecule as a whole — in that each has the same composition as all other groups and is combined with a like carbon-hydrogen atom group with two valence bonds on one side and an identical carbon-hydrogen group on the other side but with only one bond — the attack of the chlorine molecule can take place at any one of the six points of the benzene ring and exactly the same compound, monochlorobenzene, will result although the structural formulas may look differently on the page. Thus, all of the following are really the same structural formula for the same compound:

Monochlorobenzene — all four are the same formula

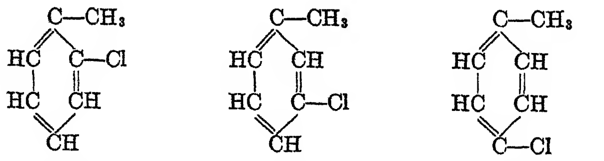


Toluene, being methyl benzene, reacts with chlorine in the benzene part of the structure in exactly the same manner as does benzene to make monochlorotoluene:

Toluene + Chlorine ⟶ Monochlorotoluene + Hydrochloric acid



But with toluene not one but three monochlorotoluenes are possible, depending on whether the chlorine atom becomes substituted on the benzene part of the molecule on the carbon atom *next* to the methyl group (*ortho position*), or on the carbon atom *next but one* to the methyl group (*meta position*), or on the carbon atom *opposite* the methyl group (*para position*). Structural formulas for these three monochlorotoluenes, together with the names applied are as follows:



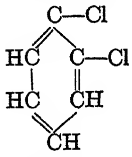
Ortho-monochlorotoluene *Meta-monochlorotoluene* *Para-monochlorotoluene*

Such chlorine atom substitutions can take place until all of the hydrogen atoms on the ring structure have been replaced.

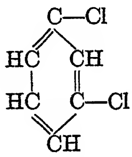
Bromine derivatives can be made in a manner similar to that used for the making of chlorine derivatives, but using bromine substance for the reaction instead of chlorine. Iodine derivatives must be made after other more involved methods than through direct reaction with iodine.

The following are structural formulas and methods of naming for some of the higher chloro derivatives on benzene and on toluene:

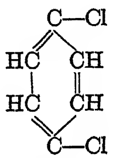
On benzene



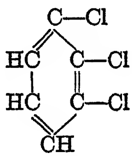
Ortho-dichlorobenzene



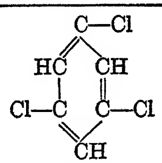
Meta-dichlorobenzene



Para-dichlorobenzene

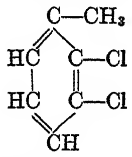


1, 2, 3-trichlorobenzene

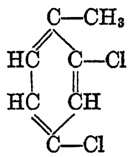


1, 3, 5-trichlorobenzene

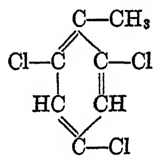
On toluene



2, 3-dichlorotoluene



2, 4-dichlorotoluene



2, 4, 6-trichlorotoluene

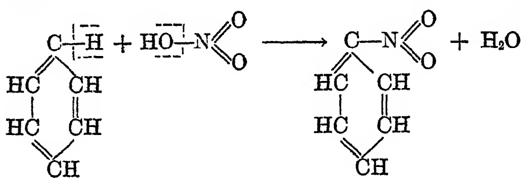
Ortho, *meta*, and *para* are naming devices used in respect to *only* two substituents on the benzene ring. If more than two substituents are present, their relative positions are indicated by numbers. *On toluene*, positions of carbon atoms in the ring structure are numbered, beginning with the carbon atom on which the methyl is substituted.

Some halogen derivatives of benzene and toluene have importance in themselves. One of these is thyroxine (p. 481) which is of vital importance and which, if made either in a greater or less amount than is normal in the thyroid gland, results in unfortunate pathological consequences. Another such derivative is tetraiodophenolphthalein which is mentioned later (p. 397). But the chemist is chiefly interested in these halogen derivatives because, once a chlorine or bromine or iodine atom gets substituted for a hydrogen atom on the benzene ring, or on any carbon atom on any

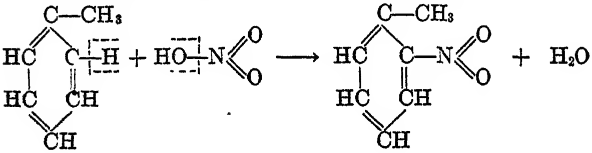
ring structure, the molecule becomes vulnerable at that point to many more attacks than with a hydrogen atom in such location.

Cyclic hydrocarbons with nitric acid to make nitro derivatives. Under favoring conditions benzene and toluene, as is true of all carbocyclics, will react with nitric acid to make *nitro* derivatives. Two such reactions are represented as follows:

Benzene + Nitric acid ⟶ Nitrobenzene + Water

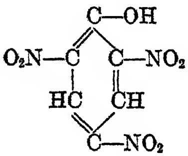


Toluene + Nitric acid ⟶ Ortho-Nitrotoluene + Water

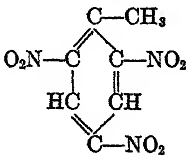


There are many important nitro derivatives of benzene, toluene, and other carbocyclic compounds. Among them is picric acid or trinitrophenol, items concerning which are given on p. 396. Some of these nitro derivatives are explosives, one of the most potent of which is trinitrotoluene, commonly called by the abbreviated name of T.N.T. Formulas for these two nitro derivatives are given below.*

2, 4, 6 ***trinitrophenol or Picric acid***



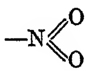
2, 4, 6 ***trinitrotoluene or T.N.T.***



Nitrite group

—O—N=O

Nitro group

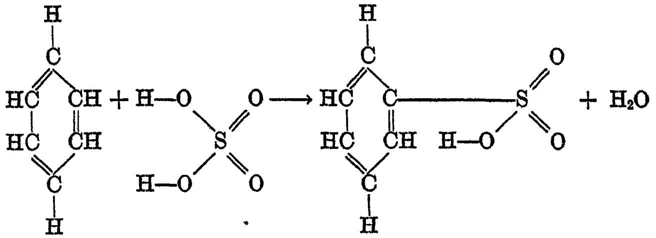


* The student should note the difference between the *nitro* and *nitrite* atom groups. Although both have the same composition and valence, hence are represented by the same empirical formula: namely, NO_2, they are re-

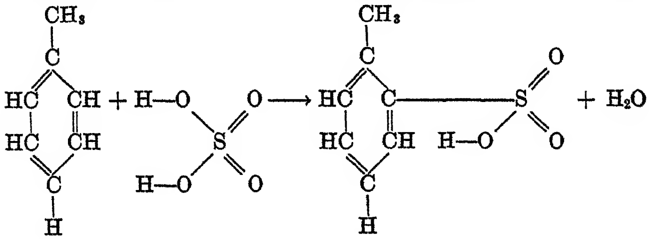
sponsible for quite different behaviors on the part of the compounds containing them, the nitrite atom group acting like the acid radical but not so with the nitro atom group. Furthermore, the nitrogen atoms within the two atom groups have different valences, that in the nitro group having a valence of five, that in the nitrite group having a valence of three. Therefore, the structural placements of the one atom of nitrogen and two of oxygen must be quite different and are believed to be according to the foregoing formulas.

Carbocyclics with sulfuric acid to make sulfonic acid and sulfo derivatives. Benzene, toluene, and other carbocyclics will also react with sulfuric acid in a manner similar to their reaction with nitric acid. If only one of the two hydroxide atom groups of the sulfuric acid molecule becomes engaged, the products are called *sulfonic acid* derivatives; if both of the hydroxide atom groups are taken from the sulfuric acid molecule, the products are *sulfo* derivatives. Such reactions with benzene and toluene are represented in the following:

Benzene + Sulfuric acid ⟶ Benzenesulfonic acid + Water



Toluene + Sulfuric acid ⟶ Ortho-toluenesulfonic acid + Water



There are many cyclosulfonic acid and cyclosulfo derivatives four of which are saccharine, phenosulfonphthalein, chloramine-T, and dichloramine-T; structural formulas for these compounds are given below. Saccharine, noted for its exceedingly sweet taste, is sometimes used, especially by diabetics, as a sugar substitute for

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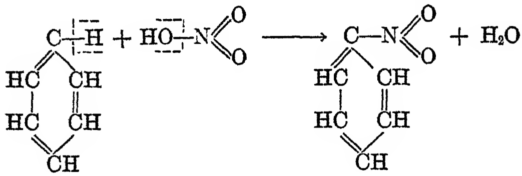
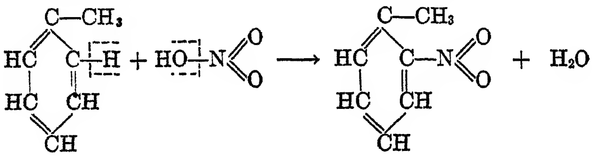


Toluene + Nitric acid ⟶ Ortho-Nitrotoluene + Water



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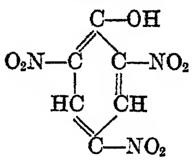
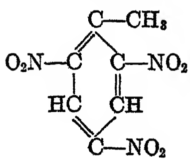


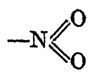
2, 4, 6 ***trinitrotoluene or T.N.T.***



Nitrite group

—O—N=O

Nitro group



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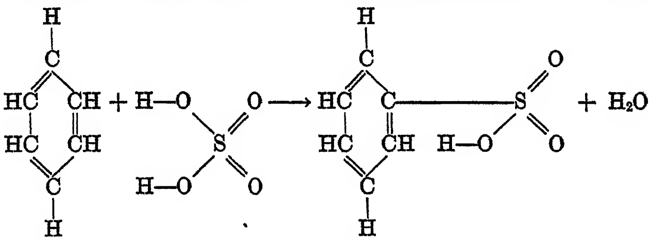
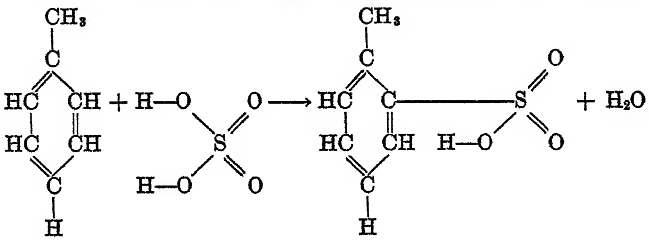


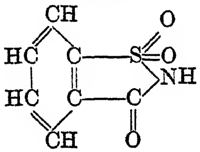
Toluene + Sulfuric acid ⟶ Ortho-toluenesulfonic acid + Water



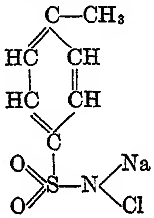
There are many cyclosulfonic acid and cyclosulfo derivatives four of which are saccharine, phenosulfonphthalein, chloramine-T, and dichloramine-T; structural formulas for these compounds are given below. Saccharine, noted for its exceedingly sweet taste, is sometimes used, especially by diabetics, as a sugar substitute for

sweetening purposes; however, a comparison of the structural formulas for saccharine and sucrose (p. 347) will show that they are in no way chemically related. Chloramine-T and the related dichloramine-T are used for the irrigation of wounds in the Dakin treatment; they are derivatives of toluene, as the T signifies. Both of these compounds owe their disinfectant action to the readiness with which they enter into various reactions to make chlorine (p. 277).

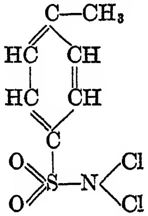
Saccharine



Chloramine-T

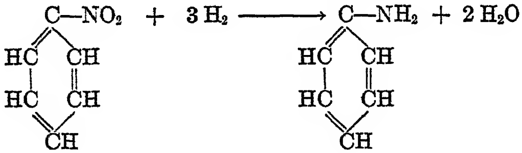


Dichloramine-T



Aniline or aminobenzene and derivatives. Large quantities of nitrobenzene are used with hydrogen for making aminobenzene, which is more commonly called aniline.

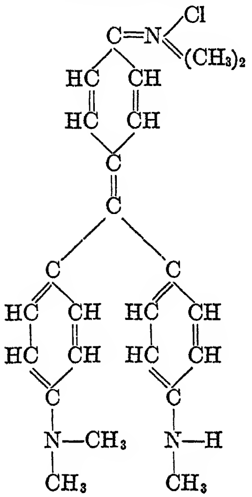
Nitrobenzene + Hydrogen → Aminobenzene + Water
(Aniline)



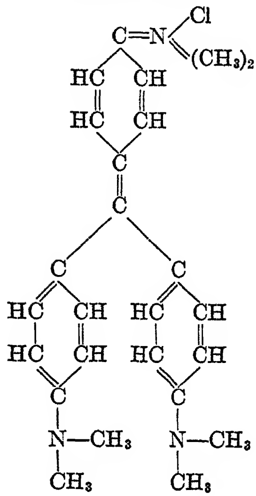
Aniline dyes. Aminobenzene is of vast commercial importance as the parent compound from which aniline dyes are made. Indeed, the first dye of coal tar origin, called mauve, which was produced on a commercial scale by its discoverer William Perkins, was made from aniline obtained from coal tar.

Three aniline dyes of importance are methyl violet, crystal violet, and methylene or aniline blue. These dyes are commonly used in the bacteriological laboratory for staining slides as a means for differentiating different strains of bacteria. The bacteriological "stain" called gentian violet is a mixture of methyl and crystal violets. Structural formulas for these three dyes reveal their aniline origin:

Methyl violet

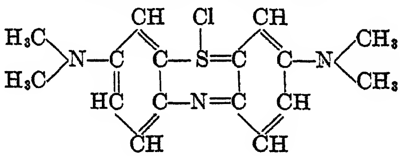


Crystal violet



Gentian violet is a mixture of methyl and crystal violets.

Methylene or Aniline blue



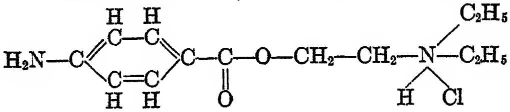
It is interesting to note that the formulas for methyl violet and crystal violet are identical save that one hydrogen atom in the former has been replaced by a methyl group in the latter; just this difference is believed to be responsible for the difference in shades of the two compounds.

Therapeutic uses. These dyes have therapeutic uses. *Gentian violet* can gain entrance to the cells of so-called Grampositive microorganisms and in so doing has a germicidal effect; therefore, it functions as a disinfectant for attacking staphylococci, diphtheria bacilli, and a variety of other microorganisms. This dye also reacts with proteins to make an insoluble compound and for this reason it is used in the treatment of burns (see p. 396). *Methylene blue* was the first of the aniline dyes to be used as an antiseptic; however, it has not proved to be very effective, hence has largely fallen into disuse for this purpose.

Drugs. Important drugs are also made *from aniline.* These include the well-known analgesic antipyretics, acetanilid and

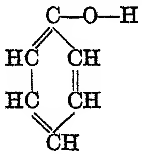
phenacetine (p. 405), also procaine (commercially known as novocaine), a local anesthetic produced in the laboratory and used as a substitute for codeine.

Procaine or Novocaine, a derivative of aniline



Phenols. When a hydroxide atom group is substituted for a hydrogen atom on a carbon within the ring structure a phenol results. This hydroxide substitution cannot be made directly from a base in reaction with the hydrocarbon carbocyclic, as from benzene or toluene, but must be made in a rather roundabout way and through a series of reactions which we shall not consider.

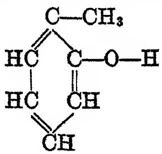
Phenol or Carbolic acid
(Monohydroxybenzene)



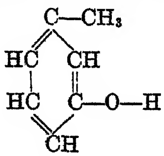
The most important of all phenols and the simplest of this class of compounds is the mono-phenol on benzene which is sometimes called simply by the class name, *phenol;* but sometimes, too, it is called *carbolic acid,* which is an appropriate name, since this compound is really an acid. This phenol is one of the parent cyclic compounds found in coal tar mixture from which it is separated for the purpose of building numerous other compounds of commercial importance, including dyes, explosives, flavors, and drugs.

Another important phenol that is derived from benzene has the structural name of meta-dihydroxybenzene and the common name, *resorcinol* (p. 396). There are three mono-phenols on toluene which are called *cresols.* Differentiating names and structural formulas for some of these compounds are as given at the left (see also p. 396).

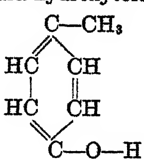
Ortho-cresol
(Ortho-hydroxytoluene)



Meta-cresol
(Meta-hydroxytoluene)



Para-cresol
(Para-hydroxytoluene)

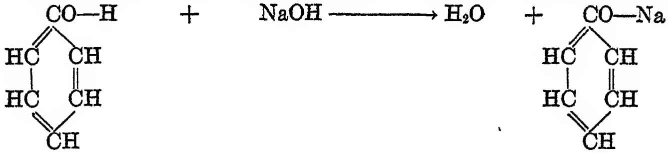


Phenols are acids. Despite the presence of the suggestive hydroxide and the ending *ol* of the name, phenols are not alcohols. On the contrary they are acids, the ionizable hydrogen atoms

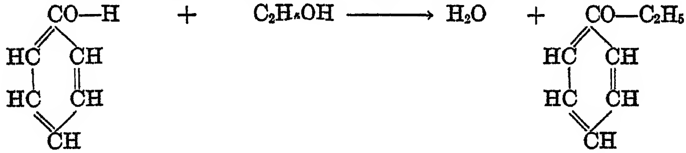
being presumably those of the hydroxide portion of the compounds not the hydrogen atoms which are attached to the carbon atoms of the ring structure. Therefore, as has already been pointed out, the name carbolic acid for monohydroxybenzene is really more to the point than phenol. It follows, then, that when phenols react with bases or with alcohols the products are water and salts or esters exactly as should be expected. Here are general statements and specific examples.

Phenol + Base ⟶ Water + Salt
Phenol + Alcohol ⟶ Water + Ester

Phenol (Carbolic acid) + Sodium hydroxide ⟶ Water + Sodium phenolate



Phenol + Ethyl alcohol ⟶ Water + Ethyl phenolate



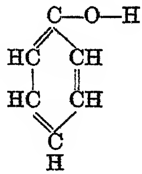
Phenols as disinfectants and antiseptics. There are a number of phenols that are known to have disinfectant or antiseptic value; six such are the subject of the following discussion.

Phenol or carbolic acid. This compound is of historical interest as the first substance used in medicine for its disinfectant effect. It was introduced in 1867 by Lister in his work in antiseptic surgery and continued to be widely used until comparatively recent years. It is a powerful disinfectant with an unusually great tendency to penetrate the tissues. Its action is due to an attack on proteins. Even in dilute solution phenol is very irritating to tissue cells and when taken internally it is extremely toxic. The principle in treating such a poisoning is to remove the caustic agent as quickly as possible, thereby decreasing the extent of the destruction. If the contact with phenol is local, as on skin or mucous membranes,

Phenol

Empirical formula: C_6H_5OH

Structural formula:

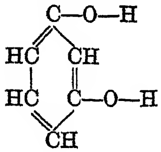


ethyl alcohol is an excellent solvent for the phenol; but if taken internally the use of alcohol is questionable since it is readily absorbed and carries the phenol along with it.[2]

But phenol, now, has been largely displaced by other disinfectants many of which can be regarded as phenol derivatives. Some of these compounds are more powerful in germicidal effect than is the parent compound (phenol) and, at the same time, less toxic. Phenol is used as a standard of comparison for other disinfectants; their activity being expressed as a phenol coefficient.

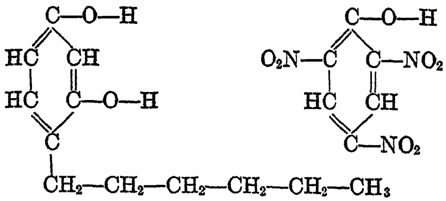
Resorcinol and hexylresorcinol are diphenols in that they have two hydroxide groups attached to carbon atoms in the ring. Both of these compounds function as disinfectants. Hexylresorcinol was introduced into therapeutic practice as a urinary antiseptic. It is now used also in the treatment of hookworm. The hexyl radical is claimed to be responsible for increasing the bactericidal effect of this compound over that produced by a shorter chain hydrocarbon combined in the same position as to the diphenol. Hexylresorcinol has a phenol coefficient of 45.[3]

Resorcinol



Hexylresorcinol

Picric acid
(Trinitrophenol)



Picric acid. The chemical name for picric acid, and the one which suggests its phenol origin, is trinitrophenol. It is used as a skin disinfectant and in the treatment of burns. Its usefulness for these purposes is due to the fact that it is capable of reacting with proteins to make insoluble compounds (p. 427). Because of its trinitrobenzene nature it is a violent explosive. Since it is used extensively in the industries, and because of its attack on the proteins of the skin and nasal passages when inhaled, picric acid constitutes another of the great industrial hazards on the part of workers who are exposed to it.

The cresols (p. 394). These phenols are more powerful disinfectants than phenol and no more toxic. Although only slightly

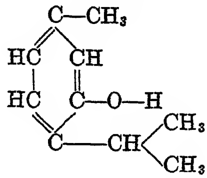
[2] L. Goodman and A. Gilman, The Pharmacological Basis of Therapeutics, The Macmillan Company, 1941, p. 829.

[3] This means that resorcinol is equally as effective as a germicide as is phenol when used in concentrations $\frac{1}{45}$ that used for phenol.

soluble in water, when mixed with soap they form either a colloidal solution or a more or less permanent emulsion, and it is in this form that they are usually encountered in disinfectant solutions. As previously mentioned, they are the principal components of lysol, also of creolin and other similar preparations that are sometimes used in homes and hospitals.

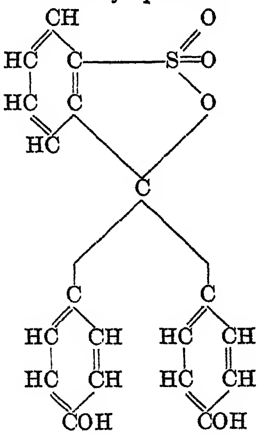
Thymol is another phenol derivative of toluene, as the accompanying formula indicates. It is found in nature as a component of oil of thyme and oil of mint.

Thymol

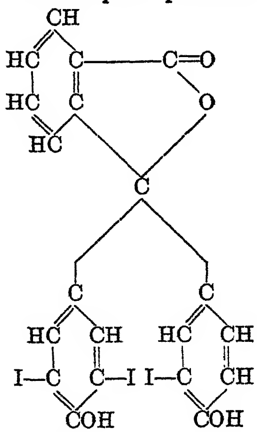


Phenol dyes used for diagnosis. Two phenol derivatives which have interesting uses as aids to the physician in making diagnostic tests are phenolsulfonphthalein and sodium tetraiodophenolphthalein. *Phenolsulfonphthalein,* when injected, is excreted more or less promptly by the kidneys; consequently, a study of the percentage of this dye which is excreted with the urine within a specified time serves as a measure of the extent to which the kidneys are functioning. The sodium salt of *tetraiodophenolphthalein,* known in hospital practice as *soluble iodophthalein,* following administration, is absorbed by the gallbladder which is thereby shown up to a greater advantage on the X-ray plate.

Phenolsulfonphthalein



Tetraiodophenolphthalein

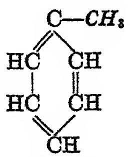
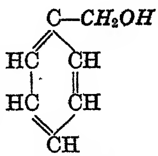
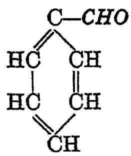
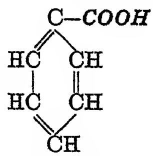
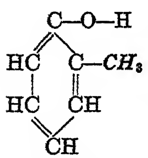
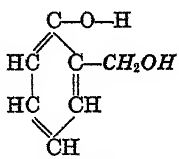
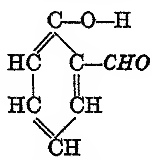
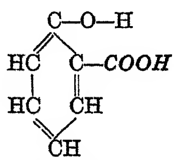


Phenols of physiological importance. Among the phenols of physiological interest are the hormone *epinephrine* or *adrenalin,* and the amino acid *tyrosine.* Epinephrine is secreted by the adrenals and among other functions plays a very important role

in carbohydrate metabolism. Structural formulas (p. 481) for these compounds show their phenol nature.

Aromatic alcohols, aldehydes, and acids. Thus far in the limited study which has been made of the chemical behavior of the aromatic compounds only that on the part of the carbocyclic structure itself has been stressed. We wish now to consider what can be expected from side chain substituents; and the fact is that *each side chain engages in reactions which are peculiar to it.* Thus, each nitro (p. 390) and each sulfonic acid (p. 391) is susceptible to side chain reactions peculiar to it quite apart from the reactions in respect to the cyclic itself. Just what the reactions are to which these particular substituent groups will respond we shall not consider. We are, however, interested in the side chain reactions when the *substituent on the ring is a straight chain hydrocarbon,* or *an alcohol, aldehyde,* or *organic acid* derived from such a hydrocarbon.

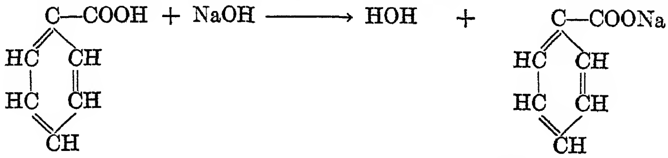
But the student of this text should be in a position to anticipate possibilities as to such reactions, since the straight chain part of the cyclic — the methyl or ethyl for example — reacts like any such hydrocarbon; likewise the primary alcohol, the aldehyde, or the organic acid substituent of these aromatic compounds reacts like any primary alcohol, or any aldehyde, or any organic acid. For example:

The methyl part of these compounds behaves like the methyl group anywhere.	*The primary alcohol part of these compounds behaves like any primary alcohol (p. 309)*	*The aldehyde part of these compounds behaves like any aldehyde (p. 316).*	*The carboxyl part of these compounds behaves like any carboxyl (p. 331).*
 *Toluene*	 *Benzyl alcohol*	 *Benzaldehyde* (Bitter almond)	 *Benzoic acid*
 *O-Cresol*	 *Salicyl alcohol*	 *Salicylaldehyde*	 *Salicylic acid*

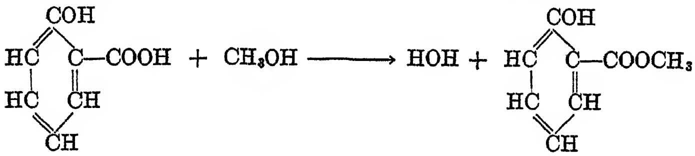
Such alcohol, aldehyde, and acid derivatives as these, in which these groups are substituted on cyclic structures, are called respectively ***aromatic alcohols***, ***aromatic aldehydes***, and ***aromatic acids.***

Aromatic salts and esters. As should be expected, aromatic acids will react with bases to make aromatic salts, and with alcohols to make aromatic esters of such acids. For example, sodium benzoate can be made from the reaction of benzoic acid with sodium hydroxide; methyl salicylate can be made from the reaction of salicylic acid with methyl alcohol. Equations for these reactions are as follows:

Benzoic acid + Sodium hydroxide ⟶ Water + Sodium benzoate



Salicylic acid + Methyl alcohol ⟶ Water + Methyl salicylate

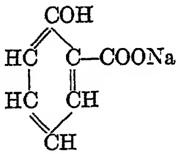
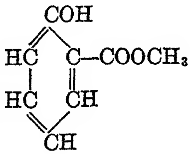
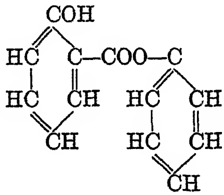
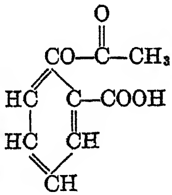


Sodium benzoate made after this manner is used as a preservative for foods; methyl salicylate made thus is synthetic wintergreen.

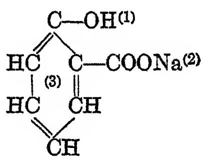
The salicylates. The salicylates form a commonly encountered family group which includes several more or less well-known compounds, some of which are given in the table on the next page.

The various salicylates have a number of common therapeutic uses. They are all regarded as having a mildly antiseptic action; they appear to have a specific value in the relief of pain of rheumatism; they are antipyretic, that is, they have an effect of lowering body temperature in fever. Salicylic acid itself is employed to a considerable extent as a corn remedy. A study of the structural formulas for the molecules of the various salicylates will clearly show the reason for their chemical similarities and differences.

Some cyclic derivatives are very complex. Some compounds of cyclic derivation are very complex indeed, depending in part upon the number and varieties of ring structures present within their molecules, and in part upon the number and varieties of side chain substituents. For example, the dyes mentioned on p. 393 and the phenolphthalein derivatives mentioned on p. 397 are fairly complex compounds, but there are other compounds not referred to in this text which are considerably more so. But it must always be remembered that, complex or not, each ring structure and each

Name of salicylate	*Formula representation*	*Use*
Sodium salicylate		Used in the treatment of rheumatism and arthritis.
Methyl salicylate		The active principle of oil of wintergreen, obtained both from this source and from synthetic preparation. Used externally as a counter irritant.
Phenyl salicylate (Salol)		Used as a coating to protect drugs for passage through the stomach; the coating hydrolyzes in the intestine, thereby releasing the desired drug.
Acetylsalicylic acid (Aspirin)		A well-known analgesic.

side chain substituent produces its own peculiar effects. This latter fact is illustrated by referring once more to the compound sodium salicylate, the structural formula for whose molecule tells that:



(1) This compound is a phenol, as indicated by the hydroxide group attached to a carbon atom in the ring, consequently sodium salicylate may be expected to behave as an acid, after the manner of all phenols.

(2) Sodium salicylate is also a salt, as indicated by the —COONa atom group, and therefore may be expected to react as a salt.

(3) It is a cyclic compound, containing the benzene ring, and hence will exhibit behaviors peculiar to the carbocyclics.

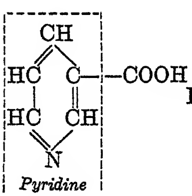
HETEROCYCLICS

As has been said previously (p. 377), compounds whose molecules contain atoms other than carbon within ring structures are known as heterocyclics, and the element whose atoms most commonly contribute to such cyclic formations is nitrogen.

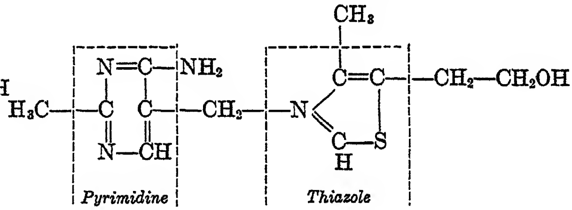
Of physiological importance. Certain of these nitrogen-containing heterocyclics, either in themselves or their derivatives, are of considerable importance physiologically. The following are examples.

Nicotinic acid, the vitamin that has proved useful in treating pellagra, is a derivative of the heterocyclic *pyridine.* This vitamin is believed to contribute to the synthesis of certain enzymes that are essential to oxidations in the cells, hence essential to normal nutrition. ***Thiamin***, or *vitamin B_1*, is a derivative of the nitrogen-containing cyclic called *pyrimidine* and the sulfur-containing cyclic called *thiazole.* It functions importantly in the metabolism of glucose and glycogen within muscle and nerve cells (p. 467). Formulas for these two vitamins are as follows, the parent heterocyclics are set off by dotted lines:

Nicotinic acid

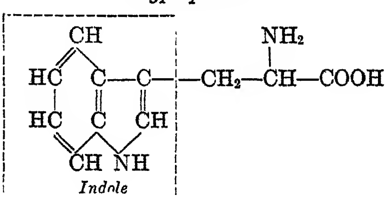


Thiamin or Vitamin B_1

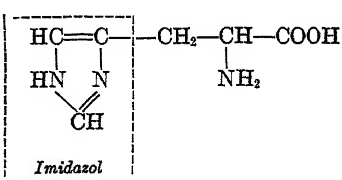


Tryptophane and ***histidine***, respective derivatives of the heterocyclics *indole* and *imidazol* are amino acids which are absolutely necessary to normal life and growth of animals; and since animals cannot build these cyclic amino acids within themselves (p. 418) they must be provided by food proteins of plant origin. These amino acids are obtained in the intestine through hydrolysis of proteins.

Tryptophane

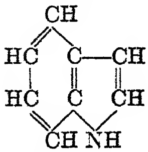


Histidine

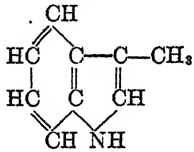


But, essential as tryptophane and histidine are, when they get to the cells, such portions as do not get absorbed are subject to attack in the intestine by certain bacteria to make *indole* and *skatole* from tryptophane, and *histamine* from histidine. It is to indole and skatole that the characteristic odor of feces is largely due. All three of these compounds are in themselves quite toxic but upon absorption nature subjects them to reactions whereby they are rendered harmless.

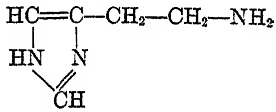
Indole



Skatole

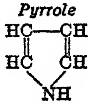


Histamine

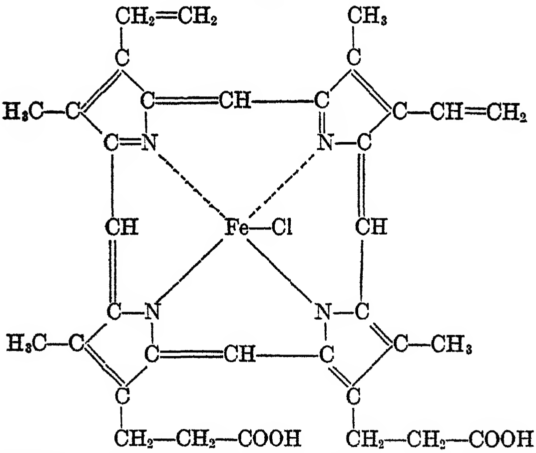


Finally, ***hemin***, derived from hemoglobin, is a tetra derivative of the heterocyclic *pyrrole*. Plant *chlorophyll* which is closely related to hemoglobin also contains pyrrole as a constituent. The formula for hemin is as follows:

Pyrrole

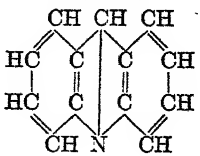


Hemin

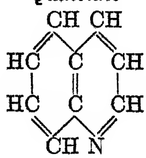


Commercial synthesis of heterocyclic derivatives. Coal tar mixture also provides heterocyclic compounds from which new compounds can be synthesized. Two such are *acridine* and *quinoline:*

Acridine

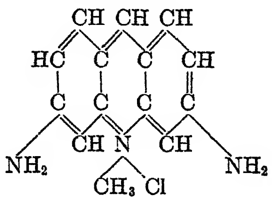


Quinoline

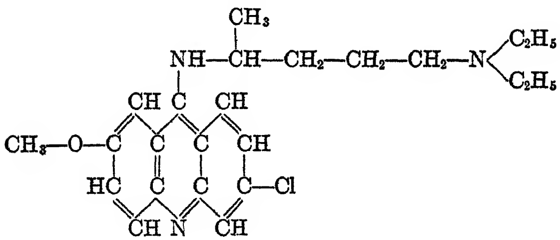


Acridine serves as the parent structure for both dyes and drugs. One of the acridine dyes is *acriflavine*, so named because of its yellow color. This compound was first used by Erlich in his search for substances that would destroy protozoa. It has been proved, however, to be more effective as a bactericidal agent and is used for dressing wounds. *Atabrine* is also an acridine derivative of laboratory origin. It promises to be useful in the treatment of certain types of malaria. Formulas for these two derivatives are as follows:

Acriflavine

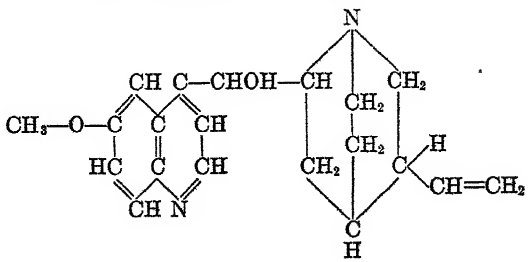


Atabrine

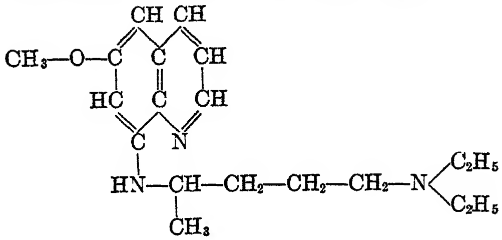


Quinine, long regarded as specific for the treatment of malaria, is a quinoline (p. 385) derivative. It has never yet been synthesized in the laboratory. However, the chemist has succeeded in producing another derivative, known as *plasmochin*, which is used to some extent as a quinine substitute. Formulas are as follows:

Quinine, obtained from bark of cinchona tree, destroys malaria organism and allays fever.



Plasmochin, a synthetic substitute for quinine.



The alkaloids. But for many of the heterocyclic compounds which produce from mild to violent physical effects man still must turn to living plants, just as have the herb gatherers since earliest times. The important group of drugs known as *alkaloids* are for the most part of natural occurrence. Thus, *morphine* is derived from the milk of the opium poppy; *atropin* from the belladonna plant; *quinine* from the bark of the cinchona tree; *caffein* from the coffee bean or tea leaves.

Chemically, alkaloids are nitrogen-containing heterocyclics. They are called alkaloids because, like alkalies, they react with acids to make salts. When used medicinally, usually the salts are prescribed, since alkaloids themselves are not soluble in water, whereas the salts made through reaction with certain acids, such as sulfuric and hydrochloric acids, dissolve readily. On the other hand, alkaloids form insoluble salts with some acids, tannic acids among them, hence the use of tannin as an antidote for poisoning by alkaloids.

SOME IMPORTANT DRUG GROUPS

Physiological effect in relation to chemical structure. In general, the physiological effect to be expected from many of the commonly used drugs has been known from ancient times. But it has remained for chemists of very recent years to begin the task of finding what these compounds are which produce such effects, to analyze them, to determine the composition and molecular weights of these compounds, and then to reason their way as to the probable placement of atoms and atom groups within molecules of the same.

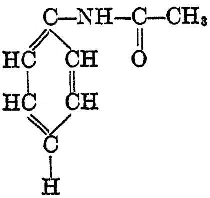
This detailed study of chemical composition and structure of molecules of compounds, together with a study of the physiological effects of various compounds, has led to the belief that certain atom groups within molecules are responsible for certain characteristic effects, while the behavior of the compound as a whole is,

in the main, a summation of these various group actions. One of the researches of the pharmaceutical chemist is that of modifying a given drug in order to increase some desired physiological effect, or do away with some undesired side effect, by removing an atom or atom group and substituting some other atom or atom group.

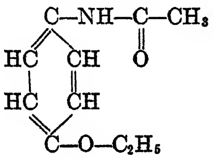
Drugs with similar effects. The following constitute a few of the well-known drug groups whose chemical structure and pharmaceutical action have come to be fairly well understood. Hence this study is designed to suggest that all drugs within any group should be studied as related compounds — where such relation exists — rather than regarded, each one, as a new and different medication.

Acetanilid, phenacetin, and pyramidon are all classed as analgesic antipyretics, meaning that they relieve pain and reduce fever. A study of the structure of their molecules suggests certain significant similarities and differences in composition.

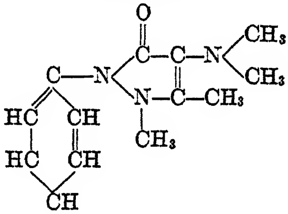
Acetanilid



Phenacetin



Pyramidon

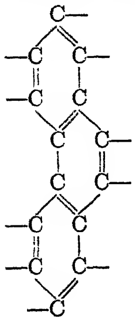


The common antipyretic effect exhibited by all three of these substances is attributed to the benzene nucleus. A similar effect is also seen in the salicylates (p. 400) whose molecules also contain the benzene ring. In their toxic effects both acetanilid and phenacetin resemble the parent compound, aniline, in that they form compounds with hemoglobin, thus interfering with the transportation of oxygen and producing cyanosis.

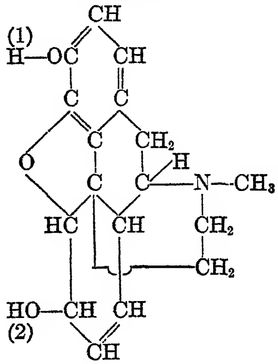
Pyramidon is not an aniline derivative as are the other two compounds. And although very much like them in physiological action and in toxic effect, it does not engage in reaction with hemoglobin. However, it has been held responsible for a destructive effect on white blood cells, known as agranulocytosis, an action not exhibited by other analgesic antipyretics.

The morphine family of drugs are narcotics. They depress the central nervous system, especially the cerebrum, and both relieve pain and induce sleep. They are all habit-forming. The most important member of the group is *morphine* which is used primarily to relieve pain. (See next page for formulas.)

Phenanthrene nucleus

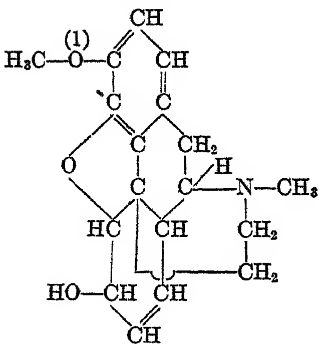


Morphine

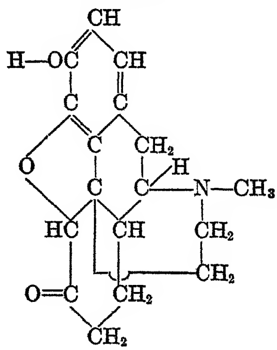


The common cyclic structure is the phenanthrene nucleus which in morphine and related drugs is combined with a side chain containing nitrogen. It is this nitrogen-containing chain which is responsible for the alkaloidal properties of these drugs. The two hydroxyl groups in morphine as designated by (1) and (2) in the above formula are also significant. Replacement of the phenolic group (1) by a meth-oxy group (CH_3—O—), as in *codeine*, reduces the analgesic effect, and the depression of respiration as observed with morphine. Replacement of the hydroxyl (2) exaggerates the narcotic effect, also the respiratory depression. Such a modification has been made in *dilaudid*. If either of these hydroxyls is replaced, the vomiting which frequently accompanies the use of morphine is decreased.[4] An important search of the pharmaceutical chemist is for some modification which will result in an effective but nonhabit-forming compound.

Codeine



Dilaudid

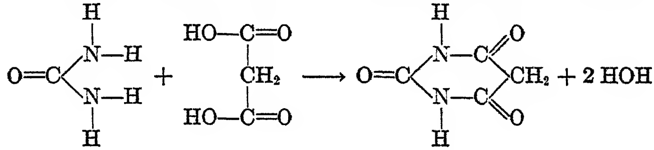


[4] L. Goodman and A. Gilman, The Pharmacological Basis of Therapeutics, The Macmillan Company, 1941, p. 187.

The alkaloids morphine and codeine are both of natural occurrence, being obtained from the juice of the opium poppy. Dilaudid is a synthetic alkaloid.

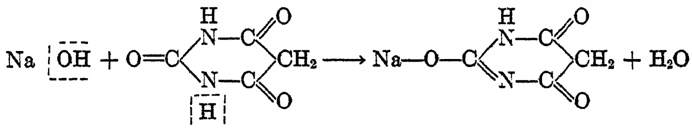
The barbiturates. These important compounds are not regarded as cyclic derivatives although their structural formulas are suggestive of such origin. Instead, they are derivatives of urea and malonic acid:

Urea + Malonic acid ⟶ Barbituric acid + Water



It will be noted that barbituric acid has no carboxyl group, but it is capable of reacting with bases to make water and salts, hence it is regarded as being an acid. The salts thus made are more soluble than the barbituric acid itself:

Barbituric acid *Sodium barbiturate*



The pharmaceutical chemist has been particularly successful in providing modifications within this drug group with the result that a great many barbituric acid derivatives are known and encountered in general use. In many instances both the barbituric acid derivative and its more soluble sodium salt are in use. It will be interesting to consider first the common behavior to be expected from any member of this group, then significant differences within various members.[5]

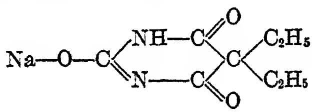
All barbiturates are sedatives and hypnotics. Some are mildly depressant and function over a long period of time; others are more powerful drugs but with a shorter functioning period; a few are depressant but quite rapidly destroyed in the body. Any of them, in large doses are respiratory depressants. The varied effects are related to chemical structure. In general, as the length of the hydrocarbon substituent increases, up to side chains of five or six carbon atoms, there is an increase in the hypnotic effect of the drugs but the period of depression is shorter. This type of modification has been achieved in *amytal*, *pentobarbital*, and *seconal*, as is evidenced in their formulas (see next page). The last-mentioned

[5] L. Goodman and A. Gilman, *The Pharmacological Basis of Therapeutics*, The Macmillan Company, 1941, p. 127.

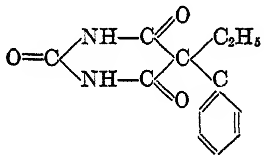
compound also contains an unsaturated radical, a constituent which increases the depressant effect of the drug. *Phenobarbital* or *luminal* contains a phenyl radical, a modification which renders this drug especially useful in epilepsy because of its anticonvulsant effect.

Barbiturates which contain the straight chain hydrocarbon and phenyl radicals are quite stable within the body, whereas those whose molecules contain more complex cyclic structures are rapidly destroyed with the result that their action is of relatively shorter duration. The following compounds are selected as typical members of the group and their formulas should be studied in reference to the foregoing discussion.

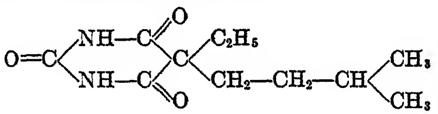
Sodium barbital or veronal takes effect in about one and a half hours after administration. Its effect wears off gradually, a feeling of lassitude often persisting for from 24 to 48 hours after administration.



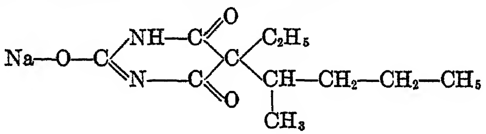
Phenobarbital or luminal also belongs to the group of long-acting barbiturates. The anticonvulsant and prolonged sedative effects make it especially useful in epilepsy.



Amytal or isoamyl ethyl barbital becomes effective in from 15 to 30 minutes after administration. Duration of action varies from 6 to 18 hours.

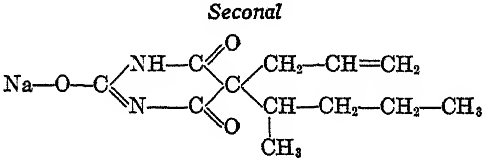


Sodium pentobarbital or nembutal also belongs to the group of barbiturates whose action is fairly rapid and of moderate duration.

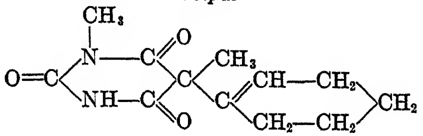


Seconal and Evipal both belong to the group whose action follows promptly upon administration but is of relatively short duration.

Seconal



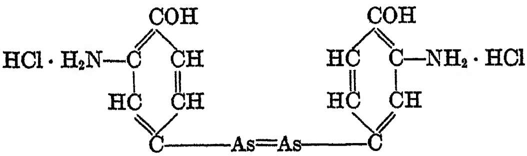
Evipal



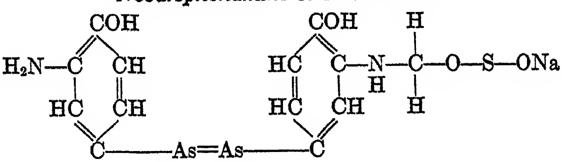
Chemotherapy.[6] One of the advances in medical science that has recently attracted considerable attention is in connection with so-called chemotherapy. This term was introduced by Paul Erlich in connection with his now famous studies of the effect of arsenic compounds on spirochetes. But the term has come to be applied to the treatment of any infection with a compound that is destructive to the invading organism without producing a serious disturbance in the host. The principle which underlies this therapy is that there should be significant differences in chemical composition and in metabolism between the host and the invading organism. *The ideal compound should be so selective as to attack and kill the invader without any injury to the host.* But there are great similarities in composition and metabolic processes in the cells of all living organisms, hence the search for suitable chemotherapeutic agents has been tedious and often unrewarding.

The first great achievement along this line was that of Erlich in the synthesis of *arsphenamine*, an arsenic compound, for the treatment of syphilis. The successful compound was number 606 in the series of substances studied for this purpose. Later, *neoarsphenamine*, number 914 in the series, came into use. The modification made was that of producing a sodium sulfonate salt as is indicated in the following formulas:

Arsphenamine or Salvarsan



Neoarsphenamine or Neosalvarsan

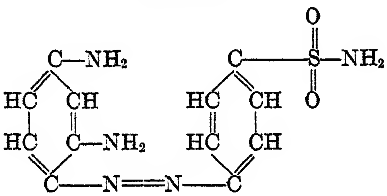


[6] An interesting discussion of this phase of medical science appears in the *Textbook of Biochemistry* by R. J. Williams, Chapter XXVIII. Van Nostrand Co., New York, 1938.

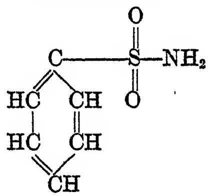
This compound is soluble in water and the reaction of the resulting solution is such as to make it more suitable for intravenous injection than the more acid arsphenamine which must be accompanied by administration of a dilute solution of sodium hydroxide.

A more recent advance in chemotherapy is the discovery of the effectiveness of *sulfanilamide* and related drugs in the treatment of various bacterial infections. The first member of this group to be used was the red dye *prontosil,* which had been discovered to be destructive to streptococci. This was used for therapeutic purposes in 1935. Shortly after this it was found that the portion of prontosil molecule that is responsible for the bactericidal action is the sulfanilamide, so the simpler compound came into use.

Prontosil

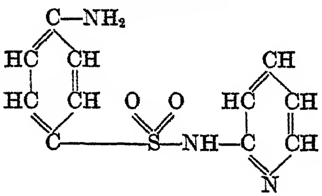


Sulfanilamide

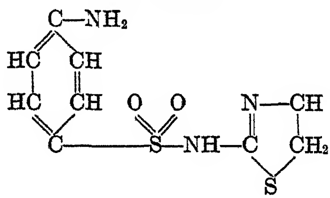


A number of related substances have been developed, the most important of which are *sulfapyridine* and *sulfathiazole:*

Sulfapyridine



Sulfathiazole



The "sulfa drugs" have proved to be very effective not only against streptococci but against other organisms as well, including pneumococci, gonococci, and meningococci, also certain of the virus infections.

The mechanism of action of these substances is not yet understood. There is some evidence to indicate that they may act to kill the invading organism; other evidence suggests that they may check multiplication of the organisms, thus making it possible for the body to mobilize its natural defenses against the infection. In giving these drugs to humans various toxic responses have been observed, some of them apparently peculiar to humans.

Chemical structure and materia medica. Students of materia medica will meet with still other groups of both carbocyclic and heterocyclic derivatives which, because of similarities and differences in chemical composition, produce at the same time similar and dissimilar effects. This information at hand will frequently simplify the study of materia medica in that it will help to place drugs into related groups. As a result, whenever a new compound appears for use as a drug, if its group relationships are recognized its general behavior when given to humans can be anticipated; thus, attention can be chiefly centered on the particular differences which this substance produces in relation to other members of the family with which the student is familiar.

Questions

1. Make a list of cyclic compounds or cyclic derivatives of your acquaintance, classifying them as to whether they are (a) "coal tar" derivatives, (b) of plant origin, (c) of animal origin.

2. What is meant by each of the following? Give an example of each by means of its structural formula and name.
   a. Cyclic compound
   b. Cyclic derivative
   c. Carbocyclic
   d. Heterocyclic
   e. Condensed cyclic

3. What is a nitro derivative, a sulfo derivative, a chloro derivative? In each case select a suitable cyclic derivative for illustration, assemble its structural formula and indicate the significant atom group. If possible cite other examples of compounds whose names indicate that they belong to any of the above classifications.

4. What is a phenol? Name several well-known disinfectants that are phenols.

5. In regard to the compounds carbolic acid and picric acid:
   a. Give another name for each.
   b. Why are these compounds called acids?
   c. What are their respective uses?
   d. What are other items of interest in respect to each?

6. Benzene and aniline are both widely used in industry.
   a. Name some of the industries in which each of these compounds is used.
   b. If workers in these industries are not afforded adequate protection from contact with these compounds, to what health hazards will they be subjected?

7. In respect to sodium salicylate, methyl salicylate, salol, and aspirin:
   a. Of what cyclic compound are these drugs derivatives?
   b. What, if any, physiological effects are common to all members of this group?
   c. How are similarities in chemical behavior accounted for? What may be responsible for differences in behavior?

8. What significant difference in the structure of the codeine molecule is believed to be responsible for the less powerful narcotic action of this drug in comparison with the effect produced by morphine? What modification in dilaudid is believed to make it a more powerful analgesic than morphine?

9. What advantage is gained in the use of sodium salts of barbituric acid derivatives over the use of the derivatives themselves?

10. What is meant by the term chemotherapy? What principle underlies the use of drugs for such purpose and why has the search for suitable drugs been so difficult? Name two drugs used successfully in chemotherapy, and specify for what function.

CHAPTER XXVIII

Proteins

Following upon carbohydrates and fats, the study of cyclic compounds might be regarded as a detour preceding our return to a study of the third great class of food substances, namely, the proteins. This detour, however, was not without purpose. Some of the amino acid constituents of proteins are cyclic derivatives (p. 416); consequently, in order to gain a clearer insight into these amino acids and the proteins containing them some knowledge of cyclic compounds is most desirable.

Biological importance and sources. The great biological importance of proteins is suggested by their very name, which comes from the Greek word meaning "of first importance." They occur in the cells of both plants and animals and are essential components of living cells. They contribute to the synthesis of protoplasm and of nucleoproteins; indeed, "there is no known life without them." [1] Proteins can be made by plant cells from carbon dioxide, water, and nitrates; but as to how this synthesis is accomplished, or what the intermediate steps may be in the process, little, if anything, is known. Animals do not have the ability to make proteins from inorganic compounds but must depend upon plants to supply them with proteins from which they are able to take constituent parts to make into compounds to meet their own specific needs. It follows, therefore, that proteins are essential components of the foods of all animals. Within the alimentary tract of the animal during the process of digestion proteins are hydrolyzed to make amino acids as end products; these in turn are absorbed into the blood stream and distributed thereby to the cells, each of which then selects such amino acids as are necessary for the building or repair of its own specific proteins and other compounds to which amino acids are essential.

Composition. All natural proteins thus far investigated are known to contain the elements carbon, hydrogen, oxygen, nitrogen, and sulfur. Many proteins, notably those occurring in cell nuclei,

[1] H. C. Sherman, *Chemistry of Food and Nutrition*, 1941, p. 42. By permission of The Macmillan Company, publishers.

contain phosphorus. Other elements may also be present in certain proteins; iron, for example, is a constituent of hemoglobin.

Molecular weights. Proteins are known to have very high molecular weights, of values which approximate 1, 2, 3, 4, etc., times 35,000. Egg albumin has been found to have a molecular weight which is probably very close to 35,000, while hemoglobins appear to have molecular weights of about 70,000 or twice 35,000.[2]

Composition of molecule and factual basis for beliefs. Let us now consider generally accepted items of belief in regard to protein molecules since — as with carbohydrates, fats, and other organic compounds — for explanation of the known composition and chemical behavior of proteins, the chemist must turn to the presumable composition and chemical behavior of their molecules. Factual evidence for theoretical deductions will be given where feasible.

1. It is believed that protein molecules are very large, hence that they are relatively very heavy; and that each molecule is composed of a very large number of incomplete amino acids in combination with each other. The belief as to the relative weights of protein molecules arises from the known very high molecular weights of such proteins as have been investigated in this respect. The belief as to their incomplete amino acid constituents arises from the fact that the end products of their reactions with water are complete amino acids.

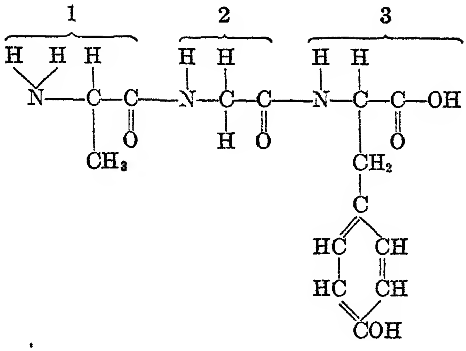
2. Protein molecules are probably very complex. This belief finds support in the fact that proteins are very difficult to hydrolyze without catalytic aid, and in the fact that no protein[3] has been synthesized to date in the laboratory despite numerous serious efforts to accomplish this feat.

3. A single protein molecule is composed of quite a number of different amino acid constituents, a belief which is derived from the experimental finding that from thirteen to seventeen different amino acids have been obtained from the hydrolysis of a single protein.

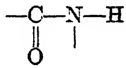
4. It is believed that within a protein molecule, amino acids are linked to each other through incomplete amino groups (each deficient in one atom of hydrogen) and incomplete carboxyl groups (each deficient in one hydroxide atom group) of adjacent acids, after the manner represented in the following:

[2] M. J. Bodansky, *Introduction to Physiological Chemistry*, John Wiley and Company, 1938, p. 106.

[3] Polypeptids which resemble proteins have been synthesized.



Representing three amino acids in combination with each other and showing two of the typical incomplete amino-carboxyl linkages:



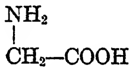
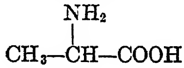
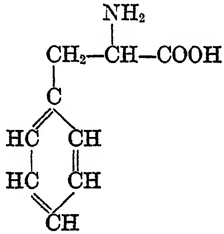
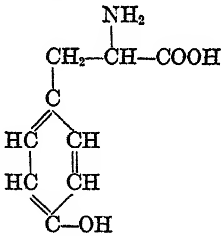
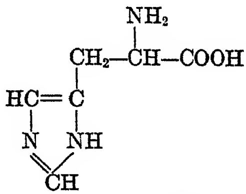
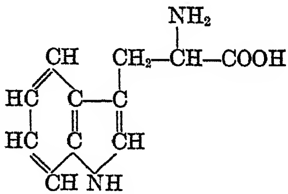
5. All natural protein molecules contain also *free carboxyl* groups through the agency of which they react with bases (p. 424), and *free amino* groups through the agency of which they react with acids (p. 425).

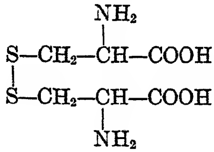
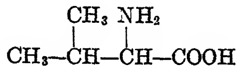
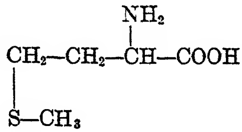
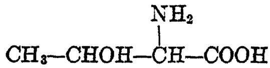
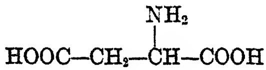
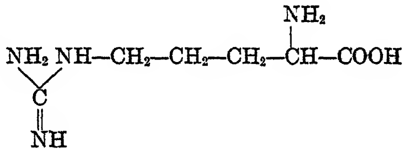
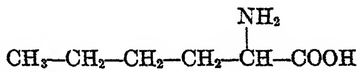
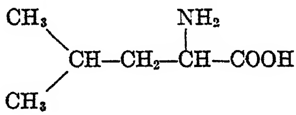
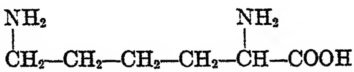
6. Linkages other than those of the amino-carboxyl type are also probably present within protein molecules and serve in part to account for their complexity.

Numerous proteins are known. According to best authorities the number of amino acids which are generally accepted to be constituents of natural proteins is about twenty-five. Other amino acids are claimed by some investigators to have been obtained by the hydrolysis of proteins, but these claims have not yet been generally accepted. However, even with only twenty-five amino acids as building stones for protein molecules, it can readily be seen that numerous different combinations of amino acids, hence numerous different protein molecules, should be possible. The situation can be compared with the assembling of words from the mere twenty-six letters of the alphabet and the thousands of meaningful letter combinations that have already been obtained therefrom. And the great number of protein molecules theoretically possible fits in with factual findings, since many different proteins have been discovered. Plants and animals build proteins peculiar to themselves; and a number, sometimes many, different proteins are made within the same plant or animal.

AMINO ACIDS

Representative amino acids. Of the authoritatively accepted about twenty-five amino acids, the following are selected as representative. They are listed in the accompanying table by their common and structural names, and the semistructural formulas for their molecules are also given:

Name	*Semistructural formula for molecule*
Glycine (α-aminoacetic acid)	
Alanine (α-aminopropionic acid)	
Phenylalanine (α-amino, β-phenylpropionic acid)	
Tyrosine (α-amino, β-parahydroxyphenyl-propionic acid)	
Histidine (α-amino, β-imidazole-propionic acid)	
Tryptophane (α-amino, β-indole-propionic acid)	

Names	*Semistructural formula for molecule*
Cystine [di(α-amino, β-thiopropionic acid)]	
Valine α-amino, β-methyl, n-butyric acid	
Methionine (α-amino, γ-methylthio, n-butyric acid)	
Threonine (α-amino, β-hydroxybutyric acid)	
Aspartic acid (aminosuccinic acid)	
Arginine (α-amino, δ-guanidine-valeric acid)	
Norleucine (α-amino, n-caproic acid)	
Leucine (α-amino, isocaproic acid)	
Lysine (α-ϵ-diaminocaproic acid)	

A study of these formulas calls attention once more to the presence of at least one carboxyl and one amino group in each amino acid molecule. However, arginine and lysine, it should be noted, are acids which contain two amino groups each; whereas aspartic acid contains two carboxyl groups in its molecule, and

cystine is both dicarboxylic and diamino. Therefore, lysine, arginine, or cystine can be linked into a protein molecule through one incomplete amino and still contribute one free amino group to said molecule; while aspartic acid or cystine can each be linked into a protein molecule through one incomplete carboxyl group and still contribute one free carboxyl group (p. 424). It is quite possible, then, that the greater number of free amino groups and free carboxyl groups, believed to be present within the protein molecule (p. 415), are due to the presence of such diamino and dicarboxylic amino acid constituents.

Constituents of substances other than proteins. Although up to the present the function of amino acids that has been stressed is that of building materials for proteins, it should be noted that nature uses them also for the making of other essential substances, enzymes and hormones among them.[4] Several digestive enzymes have been identified as amino acid derivatives and the same is true of the hormones adrenalin (p. 481), insulin, and thyroxin (p. 481).

Essential amino acids. Experimental evidence has established the fact that the animal can synthesize within itself some amino acids in sufficient quantities for its needs; glycine and alanine are two such. But there are other amino acids, known to be indispensable nutritionally for the life and normal growth of the animal, which cannot be synthesized within animal cells. Such must be provided already made within proteins of the diet. These are called essential amino acids, and according to recent findings they include lysine, tryptophane, histidine, phenylalanine, leucine, isoleucine, threonine, valine, methionine, and arginine.[5] The following are experimental findings in respect to five of these essential amino acids:

Lysine has been shown by various feeding experiments to be essential for growth, since animals fed on a diet adequate in all other respects but deficient in lysine appear to be quite normal otherwise but fail to grow. When ***tryptophane*** is not provided in the diet the animals gradually lose weight and finally die. ***Histidine,*** like tryptophane, appears to be essential for maintenance. When ***methionine*** is partially eliminated from the diet the growth of the animal is retarded; when completely eliminated the animal dies. It has been discovered, however, that cystine can be substituted in the diet for methionine up to a certain point, although it cannot entirely replace methionine. On a diet deficient in ***arginine*** the young animal maintains its weight but does not grow.

[4] Recent studies indicate that viruses are probably also protein in character.

[5] W. C. Rose, "Nutritive Significance of the Amino Acids and Certain Related Compounds," *Science*, **86**, p. 298 (1937).

This is interpreted as meaning that the animal can synthesize some arginine within its cells but not in sufficient quantity to meet the requirements for normal growth. It is for this reason that arginine is included among those amino acids which are regarded as essential.

It is quite possible that amino acids other than those listed may be necessary to normal healthy living, but conclusive evidence in this matter has not been reported.

PROTEINS (*Continued*)

Adequate and inadequate proteins. A protein which on hydrolysis provides all the essential amino acids is known as an *adequate protein*, while a protein which is deficient in one or more of the essential amino acids is known as an *inadequate protein*. For example, egg albumin and lactalbumin are adequate proteins; gelatine is deficient in tryptophane; and zein, one of the proteins of corn, is deficient in both lysine and tryptophane; hence both gelatine and zein are inadequate proteins. It must not be inferred, however, that inadequate proteins are undesirable as foods. They cannot, of course, be depended upon as the sole source of protein, but when supplemented by other proteins not thus deficient they are satisfactory components of the food mass.

Classification of proteins. So much is still unknown concerning the nature of proteins that as yet there is no clear-cut basis for classification. Such classification as has been developed is partly on the basis of certain similarities in chemical behavior and partly on the basis of similar "solubilities," meaning the tendency of proteins to form colloidal solutions in various media. There are, accordingly, three main classes of proteins: simple proteins, conjugated proteins, and derived proteins.

Simple proteins. Simple proteins are those which hydrolyze to make amino acids.[6] There are several varieties of simple proteins of which those of greatest physiological importance are the albumins, globulins, and albuminoids. *Albumins* are coagulated by heat and form colloidal dispersions in water and in dilute salt solutions. *Globulins* are also coagulated by heat and form colloidal dispersions in dilute salt solutions, but not in water. *Albuminoids* are decidedly insoluble substances in that they do not form colloidal dispersions either with water or with dilute solutions of acids, bases, or salts.

[6] Recent findings have shown a carbohydrate group to be present in some of the so-called simple proteins.

Conjugated proteins. Conjugated proteins are compounds which on hydrolysis make simple proteins and other products. Important members of this group are as follows:

1. *Nucleoproteins* are present within cell nuclei; on hydrolysis they make simple proteins and nucleic acid (p. 431).
2. *Phosphoproteins* are found in the cytoplasm of cells; they hydrolyze to make simple proteins and phosphorus-containing compounds. Caseinogen of milk and vitellin of eggs are phosphoproteins.
3. *Glycoproteins* hydrolyze to make simple proteins and glucose, or some other monosaccharid. Examples of glycoproteins are *mucin* of saliva and slippery components of other secretions; *mucoid* of cartilage and ovomucoids of egg albumin are also glycoproteins.
4. *Chromoproteins* are characterized by their color. *Hemoglobins*, as the best known examples, are the components of red blood cells which on hydrolysis yield simple proteins and an iron-containing complex called hematin. *Cytochromes* are also chromoproteins; they are present in all aerobic cells and presumably function importantly in oxidation-reduction reactions.

Derived proteins. Derived proteins are products of certain chemical changes on the part of naturally occurring proteins. Included in this group are the following:

1. *Proteoses*, *peptones*, and *peptids* are intermediate products in the hydrolysis of simple proteins.
2. *Proteans* are the insoluble proteins which result from certain enzyme actions on selected proteins of milk and blood. *Casein of milk clot*, as a first stage in the digestion of caseinogen of milk through the action of rennin, is one example of such a protein; the *clot of junket* is a protein of this variety; *fibrin of clotted blood*, made from the fibrinogen of blood, is another example of such protein.
3. *Coagulated proteins* are of two varieties, made as the result of different kinds of attack on albumins and globulins as follows:
   a. The coagulated proteins that result from subjecting naturally occurring proteins to high temperatures. The insoluble proteins that are made from the soluble proteins of egg and meat during cooking are examples of this type of coagulated proteins.
   b. The coagulated proteins that result from the reaction of alcohol with natural proteins. The reaction that takes place may involve a dehydration attack on the protein — that is, a removal of some of the protein's hydrogen and oxygen to

make water. Only concentrated alcohol functions with proteins in this manner. Any precipitation of proteins that may occur with dilute alcohol is probably physical in nature and due to their insolubility in alcohol; therefore, upon further dilution with water, the proteins will again enter into solution.

SIMPLE PROTEINS

Albumins, globulins, and albuminoids. As has been said previously, the three varieties of simple proteins that are of greatest interest physiologically are albumins, globulins, and albuminoids. *Albumins* and *globulins* are widespread in plants and animals, and they are usually associated, one or the other being in predominance. Albumins predominate in egg white and in milk. Both are present in the blood, lymph, and cytoplasm of the cells: in blood and lymph albumins predominate, while in the cells globulins are more abundant. The terms serum albumins and serum globulins are frequently used when referring to these proteins as they are found in lymph and blood plasma. The term lactalbumin is obviously suggestive of the albumin peculiar to milk. Among *albuminoids* are proteins of skin, hair, and nails, also the collagen of connective tissues. Gelatin is an hydrolysis product of albuminoids.

Solubilities and their importance. The fact that *albumins* and *globulins* form colloidal dispersions in dilute salt solutions is a property of considerable importance physiologically, also in cookery.

The blood, lymph, and contents of the cells are neutral salt solutions, a condition which insures maintenance of colloidal solution on the part of albumins and globulins there present and provides against their fatal precipitation in these locations. And the fact that these proteins are in colloidal rather than in true solution prevents them from diffusing through various membranes: they cannot normally pass from the intestine into the blood; blood proteins cannot leave that location; cell proteins cannot escape into the surrounding lymph.

In cookery, when it is desirable to have the nutritive materials from the meat cells escape into the surrounding fluid, as in the preparation of soups or stews, the meat is covered with dilute salt solution so that the albumins and globulins, along with other components, can escape from the ruptured cells to become distributed in the surrounding water.

On the other hand, and again from a physiological angle, the fact that albuminoids are insoluble in water, and in dilute acids,

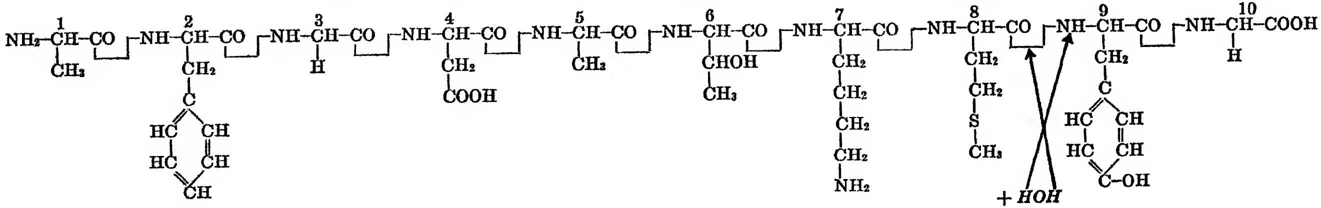
bases, and salts is of importance since this insolubility prevents the tissues of exposed areas of the body from being washed away in the course of everyday contacts with water and such solutions.

Chemical behavior and practical applications. ***Make coagulated proteins at high temperatures.*** When certain proteins are subjected to high temperatures (60° C. and above), new and insoluble compounds are made which are called coagulated proteins. The nature of the chemical change which the protein undergoes in the process is not understood.

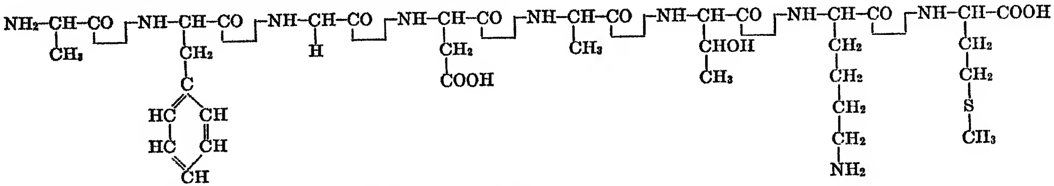
This property of proteins is of practical interest because of the part it plays in a variety of concerns. *In cookery* it is responsible for the coagulated proteins of soft and hard cooked eggs. And, in cake making, the egg proteins, previously distributed in the cake batter through beating, coagulate in the heat of the oven in locations to which they have been lifted by hot escaping gases; in this manner the cake is "lightened" and a supporting mesh is provided for all materials of the finished cake mixture. When heat is used as a *means of disinfection,* the destruction of bacteria is largely due to the coagulation of proteins within bacterial cells as a result of the high temperatures provided. In emergency this property of proteins is sometimes employed as a means for *testing for their presence in the urine;* should any considerable quantities of protein be present therein, the urine specimen, when heated, will become cloudy because of the insoluble coagulated proteins made. *In cleaning* milk bottles and dishes with clinging egg, or in cleaning clothes or linen soiled with blood stains or other protein material, this property of proteins is somewhat of a nuisance to the careless or uninformed housekeeper. The cleansing rule quite properly advises that such dishes, or clothing, or linen should first be rinsed thoroughly with cold water, or better with dilute salt solution, for carrying the proteins away in colloidal solution; whereas if hot water is used first, the proteins coagulate and the insoluble compounds thus made are very difficult to remove.

Subject to hydrolysis. Proteins are subject to hydrolysis, the end products being amino acids. These reactions are inappreciable at ordinary temperatures unless a favoring catalyst is provided. Exposure to superheated steam over a period of days, or boiling for several hours in the presence of a favoring catalyst, such as dilute hydrochloric or sulfuric acid, is necessary to produce appreciable results. In cookery processes, therefore, probably little or no hydrolysis of proteins occurs. In the cells of plants and animals, however, protein hydrolysis does occur even at ordinary tempera-

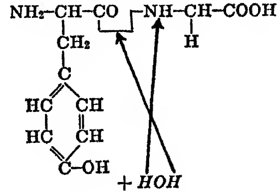
A Diagrammatic Representation of the Hydrolysis of a Hypothetical Polypeptid Molecule

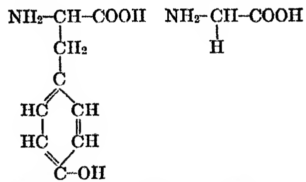


A *peptid molecule* made up of eight amino acid molecules*



A *dipeptid molecule*





Amino acids (end products)

* This peptid will, in turn, hydrolyze in stages in a similar manner to make amino acids.

Amino acid constituents of the above peptids

Alanine — 1, 5
Phenylalanine — 2
Glycine — 3, 10
Aspartic acid — 4
Threonine — 6
Lysine — 7
Methionine — 8
Tyrosine — 9

tures since various enzymes, called proteases, are provided for speeding up these reactions. The best understood of these reactions, and the best known of the enzymes concerned, are those involved with protein digestion along the alimentary tracts of such animals as have been used for these studies, including humans. The proteolytic enzymes there provided are pepsin in the gastric juice, and trypsin and erepsin found in the digestive juices in the intestines. The hydrolysis or digestive reactions take place in stages as represented in the following:

$$\text{Proteins} + \text{Water} \xrightarrow{\text{pepsin}} \text{Proteoses} + \text{Peptones}$$

$$\left.\begin{array}{l}\text{Proteins}\\ \text{Proteoses}\\ \text{Peptones}\end{array}\right\} + \text{Water} \xrightarrow{\text{trypsin}} \text{Peptids}$$

$$\text{Peptids} + \text{Water} \xrightarrow{\text{erepsin}} \text{Amino acids}$$

Keeping this known protein hydrolysis sequence in mind it becomes possible to make good reasoning guesses as to what may happen to the protein molecule on hydrolysis. Presumably successive smaller molecules with shorter and shorter chains of amino acids are made (see chart, p. 423); first proteose and peptone molecules, then polypeptid molecules, which, in turn, undergo further hydrolysis to make smaller peptid molecules and amino acids. When the tripeptid and dipeptid molecule stage is reached, further hydrolysis yields the final amino acids.

In these hydrolysis reactions, all along the way from the protein molecule down to amino acids, water molecules are believed to attack the amino-carboxyl linkages to make at each linkage a complete amino group and a complete carboxyl group, thereby severing the previously larger molecule at this point. The accompanying diagram (p. 423) attempts to suggest the manner of such reaction in respect to a peptid molecule composed of ten amino acid linkages.

Proteins are amphoteric. By amphoteric is meant that proteins are in part acids and in part bases (p. 336). ***As acids,*** in an alkaline environment, proteins react with bases to make water and salts. In this way hydroxide ions are removed and their concentration in the solution decreased. The attack, supposedly, takes place at free carboxyl atom groups in the protein molecule, as represented in the following equation, R in the formula for the protein molecule representing the rest of said molecule:

$$\underset{\text{Protein}}{\mathrm{R{-}\overset{\overset{\displaystyle NH_2}{|}}{C}H{-}COOH}} + \underset{\text{Sodium hydroxide}}{\mathrm{NaOH}} \longrightarrow \underset{\text{Water}}{\mathrm{HOH}} + \underset{\text{Sodium proteinate}}{\mathrm{R{-}\overset{\overset{\displaystyle NH_2}{|}}{C}H{-}COONa}}$$

This equation as it sometimes appears, and in the form which indicates more clearly the decrease in the concentration of hydroxide ions, is as follows:

$$\underset{\displaystyle \text{R—CH—COOH}}{\overset{\displaystyle \text{NH}_2}{|}} + \text{Na}^+ + \text{OH}^- \longrightarrow \text{HOH} + \underset{\displaystyle \text{R—CH—COONa}}{\overset{\displaystyle \text{NH}_2}{|}}$$

As nitrogen bases, on the other hand, in an acid environment, proteins react with acids, thereby decreasing the hydrogen ion concentration of the solution concerned. Just how these reactions take place is not known but, supposedly, the acids enter into combination with the protein molecules at their free amino groups. Such a reaction takes place readily between a protein and hydrogen chloride:

$$\underset{\displaystyle \text{R—CH—COOH}}{\overset{\displaystyle \text{NH}_2}{|}} + \text{HCl} \longrightarrow \underset{\displaystyle \text{R—CH—COOH}}{\overset{\displaystyle \text{NH}_3\text{Cl}}{|}}$$
$$\text{Protein} + \text{Hydrochloric acid} \longrightarrow \text{Protein hydrogen chloride}$$

If it is desired to indicate the possible manner of reaction with hydrogen ions the equation would be as follows:

$$\underset{\displaystyle \text{R—CH—COOH}}{\overset{\displaystyle \text{NH}_2}{|}} + \text{H}^+ + \text{Cl}^- \longrightarrow \underset{\text{Hydrogen protein ion}}{\underset{\displaystyle \text{R—CH—COOH}}{\overset{\displaystyle \text{NH}_3^+}{|}}} + \text{Cl}^-$$

It is believed that the hydrogen ion becomes bound to the protein molecule to make the hydrogen protein ion as indicated. In this way the concentration of hydrogen ions in a solution is decreased.

Because of this amphoteric nature, proteins of the cells, lymph, and blood exert an important *buffer effect*, helping through these counter reactions to maintain the hydrogen and hydroxyl ion concentrations in these locations within the very slightly basic range (pH 7.33 to pH 7.51) that is necessary for life and health.

With some salts to make soluble proteinates. Proteins, in their acid capacity, react with salts, after the manner of all acids, to make new acids and new salts. For example:

$$\underset{\displaystyle \text{R—CH—COOH}}{\overset{\displaystyle \text{NH}_2}{|}} + \text{NaCl} \longrightarrow \text{HCl} + \underset{\displaystyle \text{R—CH—COONa}}{\overset{\displaystyle \text{NH}_2}{|}}$$
$$\text{Protein} + \text{Sodium chloride} \rightarrow \text{Hydrogen chloride} + \text{Sodium proteinate}$$

From a physiological angle, such reactions are constantly taking place between the proteins of cells, lymph, and blood and the various salts there present; and the proteinates thus made are more stable compounds than are proteins themselves.

When reactions take place between proteins and such bases, acids, and salts as are present in the cells, lymph, and blood —

the protein derivatives that result are all of necessity *soluble* salts. But outside the body, reactions from certain of such contacts may result in insoluble salts involving proteins. A consideration of some of these reactions constitutes our next study.

With certain salts and acids to make insoluble protein salts. Some salts and acids which react to make insoluble products with proteins are soluble lead, cupric, mercuric, and silver salts; and tannic and picric acids.

Proteins with some salts make insoluble proteinates. Let us first consider the reactions of proteins with some of the above mentioned salts. When silver nitrate solution is brought into contact with a solution of protein a white, insoluble product, silver proteinate, at once appears. The reaction which takes place may be represented by the following equation:

$$\mathrm{R{-}\overset{\displaystyle NH_2}{\overset{|}{C}}H{-}COOH} + \mathrm{AgNO_3} \longrightarrow \mathrm{HNO_3} + \mathrm{R{-}\overset{\displaystyle NH_2}{\overset{|}{C}}H{-}COOAg}\downarrow$$

Protein + Silver nitrate ⟶ Nitric acid + Silver proteinate ↓

If instead of silver nitrate a solution of mercuric chloride (corrosive sublimate) is used in the same manner another heavy, white, insoluble substance will appear, this time a mercury salt, namely mercuric proteinate:

$$2\,\mathrm{R{-}\overset{\displaystyle NH_2}{\overset{|}{C}}H{-}COOH} + \mathrm{HgCl_2} \longrightarrow 2\,\mathrm{HCl} + \left.\begin{array}{l}\mathrm{R{-}\overset{\displaystyle NH_2}{\overset{|}{C}}H{-}COO}\\ \mathrm{R{-}\underset{\displaystyle NH_2}{\underset{|}{C}}H{-}COO}\end{array}\right\rangle \mathrm{Hg}\downarrow$$

Protein + Mercuric chloride ⟶ Hydrochloric acid + Mercuric proteinate ↓

It is claimed by some that salts of metals below hydrogen may also attack the protein molecule at the amino group as well as at the carboxyl:

$$\mathrm{R{-}\overset{\displaystyle NH_2}{\overset{|}{C}}H{-}COOH} + \mathrm{AgNO_3} \longrightarrow \mathrm{R{-}\overset{\displaystyle NH_2\cdot AgNO_3}{\overset{|}{C}}H{-}COOH}\downarrow$$

Protein + Silver nitrate ⟶ Protein silver nitrate

Salts which react thus with proteins to make insoluble protein salts are more or less caustic, in that when they come into contact with albumins and globulins of cell protoplasm they destroy these proteins, with the resulting death of the cells. Herein lies the basis for understanding some of the uses which are made of such salts, and some of the dangers attendant upon their use.

Uses and dangers. Solutions of certain salts are used *as disinfectants*, notably silver nitrate and mercuric chloride. Obviously

their functioning in this capacity lies in their destructive attack on the proteins of bacterial cells.

If mercuric chloride is used for disinfecting material which contains protein components along with the bacteria — such as clinical thermometers, sputum, or dressings — the salt will, of course, react with these proteins as well as with the bacterial proteins. In this case it is quite possible that the insoluble mercuric proteinate thus made, upon precipitating on surface areas, may prevent the complete penetration of the salt solution to the bacterial cells, in which case complete disinfection may not be accomplished.

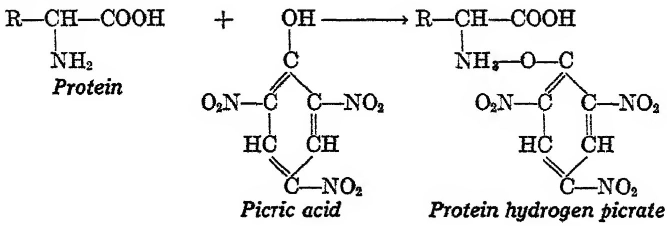
A silver nitrate (lunar caustic) pencil is sometimes used *to destroy* in similar manner the *excess granular tissue about a wound.*

The very caustic, hence *poisonous,* effect of such salts as mercuric chloride or silver nitrate when taken internally, by accident or with suicidal intent, is due to their reaction with proteins along the alimentary tract. The effect of plenty of egg albumen or milk, *as antidotes* for such poisoning, is obvious, since they provide proteins for the salts to react with instead of those of the tissue cells. The importance of immediate administration of the protein-containing antidote after such a salt is taken is self-evident. The *toxic effect* due to absorption of *lead salts,* used so extensively in paints, is believed to be due in part to the production of insoluble lead proteinates as the lead salts slowly permeate the tissues of the body.

Proteins with some such acids to make insoluble products. As for acids which react with proteins to make insoluble protein salts, the two of previous mention are picric and tannic acids, and the insoluble salts made are protein picrate and protein tannate:

$$\text{Protein} + \text{Picric acid} \rightarrow \text{Protein picrate}\downarrow$$
$$\text{Protein} + \text{Tannic acid} \rightarrow \text{Protein tannate}\downarrow$$

Supposedly, in such reactions, attack on the protein molecule is at the amino atom group, as in the reactions of proteins with acids previously presented (p. 425). There are several tannic acids, the formulas for which have not been determined satisfactorily. The presumable reaction between molecules of picric acid and protein is represented as follows:



Uses made of such reactions. This behavior of tannic and picric acids with proteins affords insight into the "why" for some of their common uses. Both picric and tannic acids are used *in the treatment of burns.* When either acid is painted over the burned area, it comes into contact with proteins of the tissue cells and reacts with them to make insoluble picrates and tannates, as the case may be. A somewhat impervious layer over the injured area is thus provided which excludes air, thereby reducing pain; at the same time the acids have a disinfectant effect in that they react with proteins of any bacteria which may have invaded the injured parts, thus destroying them. In connection with the *disinfectant property* of these acids, it should be mentioned that one of the important uses of picric acid is as a preoperative skin disinfectant. A commercial use of long standing for tannic acid is in the *tanning of hides:* the insoluble protein tannates that are made toughen the hides and are much less subject to bacterial attack and decay than are the natural proteins.

Proteins in reactions to make significant colored compounds. These reactions, as will be pointed out, are used to signify the presence either of amino-carboxyl linkages, or of specific cyclic structures. Frequently they are called protein tests, a statement which is in error since in every instance there are compounds other than proteins which give similar effects. However, it does follow, that when a positive result is obtained with any one of these reactions, it is *suggestive* that a protein may be present; and if the material under investigation responds to several of these reactions, the likelihood that a protein is present is increased. But the chief value of these reactions to the chemist lies in the fact that, when applied to compounds *known* to be proteins, positive responses, made evident by the appearance of the suggestive colored compounds concerned, signify the presence of definite amino acid constituents, whereas negative responses signify the absence of these specific constituents.

The biuret reaction. The procedure for obtaining this reaction calls for adding to the dilute protein dispersion under test, first a drop or two of sodium or potassium hydroxide to provide the requisite basic environment, then a few drops of dilute copper sulfate solution. A complex compound of unknown composition is made which varies in color from blue-violet to red-violet. In general, the blue-violet compound is obtained with proteins, whereas the red-violet compound is more significant of peptones and peptids. The reaction is reported as being *significant of at*

least two amino-carboxyl linkages, hence it applies to all proteins and their hydrolysis products down to and including, tripeptids. It functions only with proteins in colloidal dispersion not with insoluble proteins such as albuminoids and coagulated proteins. It is also unreliable if colored compounds are present.

Since the biuret reaction is specific for the linkages mentioned, it would follow that it gives positive response, not only with proteins and their intermediate hydrolysis products, but with all compounds which contain said linkages. Among such compounds is the one called biuret from which the reaction derives its name. The formula for biuret is as follows:.

$$\begin{array}{l} NH_2\text{—}CO \\ \qquad\quad | \\ \qquad\;\; NH \\ \qquad\quad | \\ NH_2\text{—}CO \end{array}$$

Xanthoprotein reaction. When a protein, either soluble or insoluble, comes into contact with nitric acid, a compound, lemon-yellow in color, is made. If in an alkaline environment, as would be the case if sodium or ammonium hydroxide were added, this color deepens to an orange. It is from xanthoprotein, meaning *yellow-protein,* thus made that this reaction derives its name. The yellow stain that appears when nitric acid is spilled on the skin, or on wool or silk, is due to this reaction.

If the protein is in solution in a test tube, and if nitric acid (concentrated) is poured carefully down the side of the tube, the precipitated yellow-protein appears in a ring formation, called *Heller's ring,* at the junction of the two liquids. This procedure is frequently used for testing the possible presence of proteins in the urine.

A positive reaction in this procedure — that is, the appearance of xanthoprotein — is *indicative of the benzene nucleus,* hence signifies the presence within the protein of one (or all) of the three amino acid linkages which contain said nucleus: namely, phenylalanine, tyrosine, or tryptophane. And since all natural proteins do respond to this test it signifies that they do contain one or all of these amino acids.

But mention should be made of the fact that compounds, other than proteins, which contain the benzene ring also make yellow compounds when treated with nitric acid: picric acid (p. 396) is such a yellow nitrobenzene derivative.

Millon's reaction. A third reaction which is employed in the study of proteins is called Millon's reaction, the reagent in this

instance being a mixture of mercury compounds. When this reagent is mixed with a protein and heated, a reddish, insoluble compound of unknown composition is made, *providing the protein contains the tyrosine amino acid linkage,* and most natural proteins do contain tyrosine. Pure gelatine, however, does not contain this amino acid linkage, consequently this protein does not give a positive response to this reaction.

Millon's reaction is not really a test for tyrosine but rather for the monohydroxybenzene ring which is one of its constituents. It follows, then, that compounds other than proteins which contain this structure are able to respond to this reaction.

Hopkins-Cole or glyoxalic acid reaction. The reagent used in this reaction is glyoxalic acid (formula CHO—COOH), and a positive response to the reaction, as described below, indicates the *presence of indole* as a constituent of the compound under test. The procedure is as follows. Equal quantities of glyoxalic acid solution and the solution of material under investigation are mixed in a test tube. Then concentrated sulfuric acid is poured carefully down the side of the tube, held in a slanting position, in such a way that the denser acid does not mingle with the solution but settles as a distinct layer beneath it. If the compound under test contains an indole constituent, a delicate violet ring appears at the junction of the two liquids (Fig. 90). If, therefore, said compound is a protein a positive response signifies the presence of the one amino acid known which does contain indole: namely, tryptophane. All adequate proteins do contain tryptophane; gelatine, however, which is deficient in this amino acid as well as in tyrosine, does not react with glyoxalic acid in the manner described. The nature of the reaction is not known but inasmuch as indigo, which is blue, is known to be oxidized indole, it is conjectured that possibly the glyoxalic acid may oxidize the indole portion of compounds containing it, such as tryptophane, to make other compounds which approximate the blue color of indigo. The following formulas for indole and indigo, also for tryptophane are suggestive of this relationship:

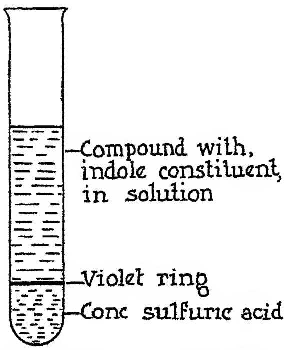
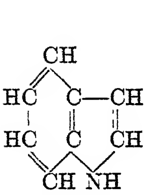
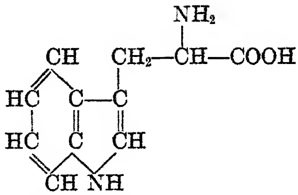


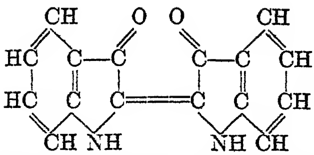
Fig. 90. With Hopkins-Cole Reagent



Indole



Tryptophane



Indigo (*oxidized indole which is blue*)

Tryptophane oxidized in similar manner presumably results in a compound with a color that is suggestive of that of indigo.

TWO CONJUGATED PROTEINS

Nucleoproteins. Nucleoproteins are present within the nuclei of both plant and animal cells. It is not known with certainty whether or not they also occur in the cytoplasm. They are especially abundant in the tissues of such glands as are rich in nuclear material: notably the liver, spleen, pancreas, thymus, and kidney, also in muscle tissue. In the plant family they are present in the germ of grains, and they are very abundant in yeast cells.

Hydrolysis products. It is known that certain differences exist between nucleoproteins of plant cells and those occurring in animal cells. But all nucleoproteins are conjugated proteins which on hydrolysis yield simple proteins and nucleic acid. Nucleic acid on further hydrolysis yields phosphoric acid, a monosaccharid, two purines — usually adenine and guanine — and two pyrimidines. Purines and pyrimidines are nitrogenous compounds of the cyclic variety.

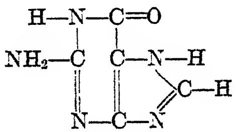
Nucleoprotein + Water
↓
Simple protein + Nucleic acid

Simple protein + Water → Amino acids

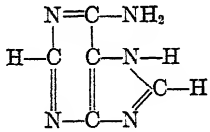
Nucleic acid + Water →

Phosphoric acid + Monosaccharid + Purines + Pyrimidines
(Adenine)
(Guanine)

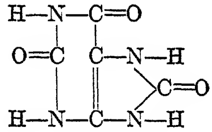
Of pathological interest. Little is known concerning the biological aspects of purines, and even less concerning pyrimidines. But it is known that in humans purines are deaminized and oxidized in cells somewhere in the body to make uric acid which is eliminated in the urine. The composition and relationship between guanine and adenine and their metabolic end product, uric acid, is suggested in the following formulas:



Guanine



Adenine



Uric acid

In this making of uric acid lies a difficulty of occasional concern, since in certain pathological conditions, notably in gout, because of the slight solubility of uric acid in body fluids, it becomes in part deposited around the joints.

Hemoglobins. Hemoglobins are characteristic of all vertebrate animals. The number of these proteins is large, every animal having hemoglobins that are quite characteristic of it. More than one hemoglobin may occur in each animal species, for example: there is evidence that blood and muscle hemoglobins of humans are different but related substances. Although there are so many of these conjugated proteins, the iron-containing constituent, hematin, that is characteristic of hemoglobins, is believed to be the same for all (p. 402), the essential difference in their composition being due to different amino acid complexes which make up the simple protein parts of hemoglobin molecules.

In all animals the function of hemoglobin is the transportation of the substance oxygen to the cells. When hemoglobin comes into contact with oxygen from the air at lung cells a direct combination reaction takes place and oxyhemoglobin is made. Then at the cells, where oxygen is needed for making various energies, the reverse reaction takes place (pp. 505, 507).

Substances other than oxygen can also engage in reaction with hemoglobin. Thus, potassium chlorate, potassium permanganate, and other oxidizing agents react with it to make stable compounds known as methemoglobins. Such oxidations are not reversible, hence these substances are toxic. Carbon monoxide combines with hemoglobin to make stable compounds as do hydrogen sulfide and hydrogen cyanide; and this prevents the normal functioning of hemoglobin as an oxygen carrier.

SUMMARY OF PHYSIOLOGICAL IMPORTANCE OF PROTEINS

Of food proteins. They provide amino acids for the building of body proteins and other substances of physiological importance: notably enzymes, vitamins, and hormones.

Of body proteins. 1. They contribute to the synthesis of nucleoproteins and protoplasm.

2. They provide reacting partner substances for oxygen in the cells for making energies that are essential for living needs.

3. They function as buffer substances in maintaining the normal hydrogen ion concentration, in the blood, lymph, and cells, which is compatible with life and health.

4. They probably function as emulsifying agents, thereby helping to keep any fats present in a condition of permanent emulsion.

Questions

1. What factual findings indicate the biological importance of proteins?

2. A great many different proteins are known, each species of plant or animal building its own specific varieties of proteins. How is this fact explained theoretically?

3. Assemble a semistructural formula representation for a hypothetical peptid molecule showing: (a) at least five different contributing amino acids, (b) several amino-carboxyl linkages, (c) two or more free amino atom groups and two or more free carboxyl atom groups.

4. From the nutritional angle what is an adequate protein? Give examples. What constitutes an inadequate protein? Give examples. Can inadequate proteins be included in a well balanced diet? Explain.

5. What is meant by a simple protein? A conjugated protein? A derived protein? How do these proteins differ? Name several examples of common proteins belonging to each class.

6. Keeping in mind the "solubilities" of various simple proteins and their behavior on being subjected to high temperatures explain each of the following:
   a. The disinfectant effect of high temperatures.
   b. The best procedure for the removal of egg stains, blood stains, and mucous secretions from fabrics.
   c. How the presence of eggs in the batter affects the leavening of cake or muffins.
   d. The procedure for treating meat in the making of soup or stew.
   e. The treatment for steaks, roasts, etc. when it is desired that the nutrient material be retained within the meat cells.

7. What is meant by the statement that proteins are amphoteric? How does this property enable them to function as "buffers"? Illustrate by means of equations the possible reaction on the part of the protein upon introduction into the solution of an acid. Of a base.

8. From the standpoint of the protein involved account for:
   a. Why salts of heavy metals are poisonous. Name several such salts.
   b. The action of white of egg or milk as an antidote for any of the above mentioned poisonings. Why is prompt administration essential?

c. The use of mercuric chloride as a disinfectant.

d. The use of the silver nitrate pencil for destroying excess granular tissue about a wound.

e. The functioning of tannic and picric acids in the treatment of burns.

9. Egg albumin, when subjected to the following tests, gives positive results with each — Biuret, Millon, Xanthoproteic, Hopkins-Cole. What information is thereby provided concerning the composition of this protein? Gelatine, when subjected to the same tests, fails to give a positive result with either the Millon or Hopkins-Cole reagent. What information is thereby provided concerning this protein? Of what nutritional significance has this finding as to gelatine?

CHAPTER XXIX

Chemistry of Digestion

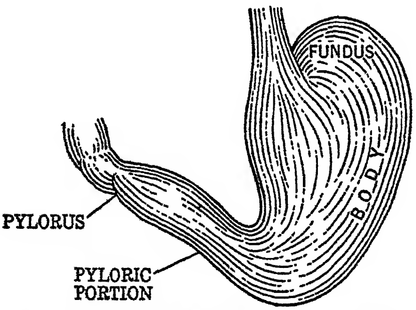
When most people talk about *food* they are referring to materials on the plate, some of which when taken into the digestive tract serve as the source of various substances necessary to life and health, some of which do not serve this important end but are eliminated as such directly from the alimentary canal. Yet this concept of food does not include one essential substance which must enter the body by a route other than from the intestine, and without which the vital reactions going on in the cells cannot take place. This substance is, of course, oxygen, which enters by way of the lungs. But the physiologist looks upon food, with an eye to cell needs, as those substances which, when taken into the cells, either (1) provide the energies necessary for living, or else (2) provide materials for the synthesis of substances essential for protoplasm or for the regulation of body processes. From this standpoint food does include oxygen; it also includes essential glucose, fats, proteins, water, certain salts, and vitamins.

Because of these two different concepts as to what constitutes food, and in order to avoid confusion in the discussion to follow, let us use the term *food* in the stricter cell need sense of the physiologist, making use of the expression *food mass* to designate the crude mixture on the plate or in the alimentary tract.

What is digestion? In the food mass of the usual diet are some substances, salts and glucose among them, which are ready for absorption and transportation to the cells. But making up the greater portion of this food mass are various carbohydrates, fats, and proteins which are not available for absorption but must undergo chemical changes to make substances which can be absorbed into the blood and lymph and used by the cells. These chemical changes, however, are not so easy to accomplish, for reasons that will become evident as this study advances, and must be preceded by the preparation of carbohydrates, fats, and proteins for said changes through various physical agencies. *It is the sum-total of these processes, both physical and chemical, that is called digestion.*

Physical processes of digestion. The physical processes of digestion include such factors as (1) motility, which provides for the thorough mixing of the contents along the alimentary tract; (2) provision for obtaining various substances in true or colloidal solution or emulsion; (3) the extensive provision for absorption; and (4) the considerable time that the food mass remains in the alimentary tract, which depends upon the motility of the alimentary tract and upon the effectiveness of absorption. These digestive factors are considered in some detail in the following.

In the mouth, mastication of the food mass breaks it up into smaller particles and mixes it with the saliva. This begins the process of providing for a large area of contact of the food mixture, first with the saliva, later with the other digestive juices, a condition most favorable to the progress of all chemical reactions. At the same time the food mass becomes lubricated by mixing with water and slippery mucin, both of which are components of saliva, thus making the swallowing process easier. Following the act of swallowing, the food mass passes along the esophagus to the stomach, its passage being aided by the peristaltic contractions of the esophagus.



From *Textbook of Anatomy and Physiology*, by Kimber, Gray and Stackpole. By permission of The Macmillan Company, publishers.

FIG. 91. The Stomach

In the stomach. Soon after this food mass enters the stomach the strong muscular walls of that organ set up contractions which "churn" the food mass, breaking it up into still smaller particles and thoroughly mixing it with the gastric secretion, thereby continuing the process of obtaining a still larger surface of contact between the food mass and the digestive secretion. Most of the mechanical action goes on in the pyloric portion of the stomach, the peristaltic contraction originating about the middle of the organ and traveling toward the pylorus. The fundus region of the stomach is much less active and serves as a reservoir from which portions of the digesting mass are gradually passed on to the more motile regions. From time to time as digestion progresses, a stimulus is set up which causes the pyloric valve guarding the entrance to the duodenum to open and allow some of the material

from the stomach to enter the small intestine. Due in part to the thorough mixing of insoluble substances with water, and in part to the making of more "soluble" substances through chemical changes already accomplished, the partially digested mixture leaving the stomach is, for the most part, in a liquid or semiliquid condition. The time required for the passage of a meal through the stomach varies from about two to seven hours. There is evidence that gastric motility decreases with a deficiency of vitamin B_1 (thiamin) in the diet. There is also a decrease in appetite under such a deficiency.

In the intestine, the food mass is subjected to still further muscular activity, the peristaltic movement of the intestine carrying it in wavelike motion forward and back but nonetheless steadily onward along the digestive tract. Another movement, described as rhythmic segmentation, keeps breaking the mass up into new segments. These two varieties of motion render digestive aid in several ways:

1. The insoluble substances are separated into finer and finer portions throughout the intestine.
2. The getting-into-solution of such substances as can enter into either true or colloidal solution is greatly aided.
3. The emulsification of bothersome but essential fats is promoted.
4. All materials are propelled and distributed along the intestine.

These processes accomplish two important ends. They increase further, and very greatly, the area of contact between still undigested components and the digestive juices within the intestine; and they promote the absorption of digested end products by bringing them into contact with the extensive area of absorbing membranes. Other favorable conditions which these intestinal movements bring about are the following:

5. First, the considerable pressure exerted on the intestinal membrane forces the blood and lymph, laden with absorbed end products of digestion, from the capillaries and lacteals of the villi into the larger blood vessels and lymphatics; then the alternate release of this pressure favors the inrush of new blood supplies to pick up new supplies of digestive end products. In this manner absorption is carried continuously forward throughout the small intestine.
6. Finally, the undigested residue is carried into and along the large intestine, from which it is eliminated.

The passage of the food mass along the intestine is relatively slow, usually requiring from six to twenty-four hours in the small intestine, and normally about eighteen hours in the large intestine. The reason why these mixings, and the obtaining of substances in true solution, in colloidal solution, or in emulsion are aids to chemical reactions has already been considered. That the *time* during which the food mass is held in contact with digestive secretions is also an important factor in chemical digestion is obvious. But both of these digestive factors — mechanical and time — will be stressed again and yet again as the reactions involved in chemical digestion are studied. Just why *proper absorption* is a necessary adjunct toward carrying chemical digestion to completion and why poor absorption speeds down the reactions concerned remain to be considered (p. 454). For more detail as to the physical processes of digestion the student is referred to books on physiology.

CHEMICAL DIGESTION

Digestion may quite properly be said to begin with the cooking process. At baking and toasting temperatures, a very small portion of any starch may possibly be hydrolyzed to the dextrin-maltose stage. In baking and broiling, small portions of fats which are exposed to the higher temperatures thus obtained may hydrolyze. Protein connective tissues are softened during cooking procedures and their albuminoid collagen is hydrolyzed to gelatine; muscle tissues of the food mass are thereby rendered more pervious to the later penetration of digestive secretions, and the gelatine made is subject to a later spreading-out in colloidal solution in the alimentary tract, whereas collagen is not. Proteins are probably not hydrolyzed in cookery to any extent aside from this above mentioned reaction on the part of collagen. But in addition to these very limited physical and chemical digestive processes, cookery further promotes digestion by rendering the food mass more pleasing to smell, sight, and taste, in this way setting up a reflex stimulation favorable to the secretion of saliva and gastric juice preparatory to the reception of the foodstuff for digestion.

By far the greater portion of chemical digestion remains to be continued and completed during salivary, gastric, and intestinal digestion. However, since the chemical changes which compounds of the food mass must undergo in the digestive tract are rendered appreciable only through the agency of specific enzymes, and since these enzymes have not been considered previously,

it seems advisable to delay still further a more detailed study of chemical digestion in order to stress a few items in regard to enzymes.

Digestive enzymes. Enzymes in general are catalysts which are made in the cells of plants, animals, and bacteria. Being catalysts they affect the speed of the particular reactions in respect to which they function, without themselves seemingly becoming otherwise involved (p. 59). It follows, therefore, that an enzyme is able to function over and over again, thereby speeding up the reaction of enormous quantities of the substances concerned. One important property of enzymes, in contrast with inorganic catalysts, is that they are destroyed at only moderately high temperatures; a temperature of 70°–80° C. is reported as resulting in rapid destruction of enzymes in general, although some of bacterial origin are more resistant and for short periods can withstand temperatures even as high as 100° C. Nature is lavish in the making of enzymes, and needfully so, since most of the numerous reactions that take place within the cells of plants and animals are complicated and would be negligible in speed without their aid.

Reactions that are essential for life activities of bacteria are also favored by enzyme catalysts. In fact, many of the metabolic reactions of bacteria are very similar to those that take place in animals, hence they require the same enzymes. But with these very limited preliminary observations in regard to all enzymes, let us turn now to the specific enzymes which are made for speeding up the various digestive reactions.

Within recent years considerable research has been done with the purpose of discovering the nature and origin of these enzymes and to determine what factors influence their activity. In summarizing these findings concerning their nature and origin Sherman states,[1] "There is now no good reason to doubt and abundant reason to accept the conclusion that the best studied enzymes of the digestive tract are amino acid derivatives of protein or protein-like nature and that food protein furnishes amino acids to serve as material for body enzymes as well as for body tissues in the more familiar sense."[2]

Among the factors which are claimed to affect the functioning of these digestive enzymes are the following:

[1] H. C. Sherman, *Chemistry of Food and Nutrition*, 1941, p. 90. By permission of The Macmillan Company, publishers.

[2] Northrop succeeded, about 1930, in securing crystalline pepsin and crystalline trypsin and demonstrated their protein nature. More recently it has been found that salivary amylase (ptyalin), pancreatic amylase (amylopsin), and pancreatic lipase (steapsin) all respond to protein tests.

1. Each enzyme functions best within a rather limited hydrogen ion concentration range, any variation from which either retards the activity of the enzyme or destroys it. Optimum conditions in this respect which have been reported for some of these enzymes will receive attention later (p. 455).

2. For some, perhaps all, enzymes it appears that the presence of specific salts or salt radicals is essential for their optimum activity.

3. Another essential calls for the removal of the hydrolysis products of the reaction for which the enzyme functions (p. 454).

With these and any other necessary favoring conditions obtained, it would seem to follow that a digestive enzyme should be able to catalyze the reaction of enormous quantities of the food substances concerned; and it is known that this is possible with pancreatic amylase which when purified has been found to catalyze 4,000,000 times its weight of starch before being destroyed.[3] But despite their efficiency these enzymes are organic compounds and unstable, especially in solution. Perhaps this is the one reason why under optimum conditions they do not continue their catalytic activities indefinitely.

Salivary digestion. ***The saliva.*** In the mouth the food mass comes in contact with the first of the digestive juices. Saliva is secreted, from substances obtained from the blood stream, by the parotid, sublingual, and submaxillary glands whose ducts empty into the oral cavity. Its secretion is stimulated both by psychic stimuli such as pleasing sight, smell, or even thought of food, and by the mechanical stimulus of mastication. It is surprising to learn that from 1000 to 1500 cc. of saliva is normally secreted daily, the quantity varying somewhat according to the nature of the food mass and the length of time of mastication. Acids and condiments, and lengthy mastication markedly stimulate secretion; dry and bland foods, and brief chewing have only a moderate effect.

The principal components of whole saliva are as follows: water which comprises over 99 per cent of the whole; albumins and globulins, and mucin which is the glycoprotein responsible for the slippery character of the saliva; salts, notably potassium chloride, potassium phosphates and carbonates; and the enzyme ptyalin or salivary amylase. The hydrogen ion concentration of whole saliva is usually neutral, or slightly on the acid side. It varies somewhat in different individuals and in relation to mealtime but is commonly found to range between cH $10^{-5.75}$ to $10^{-7.05}$ (pH 5.75–7.05). This

[3] H. C. Sherman, *Chemistry of Food and Nutrition*, 1941, p. 84.

fairly constant hydrogen ion–hydroxyl ion concentration is maintained within this small range through the buffer reactions of salts after the manner described on p. 492.

Saliva performs two functions in the digestive processes; it begins chemical reactions on the part of starches due to the catalytic action of ptyalin, and it assists in swallowing due to the lubricating effect of the large quantity of water and the slippery mucin provided.

Reactions involved. The reactions involved in *salivary digestion* are believed to be hydrolytic in nature and they are known to take place in sequence as represented by the following word equations:

Starches + Water → "Soluble" starch + Maltose
"Soluble" starch + Water → Erythrodextrins + Maltose
Erythrodextrins + Water → Achroodextrins + Maltose

Taking this reaction sequence as the basis for the guess, the possible fate of a single molecule of starch in the process of hydrolysis may be, in part at least, as represented by the following series of equations.[4] A hypothetical starch molecule composed of twelve incomplete maltose molecules has been arbitrarily selected for this representation:

$$
\begin{array}{l}
\underset{\textit{Starch}}{(C_6H_{10}O_5 \cdot C_6H_{10}O_5)_{12}} \\
\quad \downarrow + 2\,HOH \\
\underset{\textit{Soluble starch}}{(C_6H_{10}O_5 \cdot C_6H_{10}O_5)_{10}} + \underbrace{2\,C_6H_{11}O_6 \cdot C_6H_{11}O_5}_{\textit{Maltose}} \\
\quad \downarrow + HOH \\
\underset{\textit{Erythrodextrin}}{(C_6H_{10}O_5 \cdot C_6H_{10}O_5)_{9}} + \underbrace{C_6H_{11}O_6 \cdot C_6H_{11}O_5}_{\textit{Maltose}} \\
\quad \downarrow + HOH \\
\underset{\textit{Erythrodextrin}}{(C_6H_{10}O_5 \cdot C_6H_{10}O_5)_{8}} + \underbrace{C_6H_{11}O_6 \cdot C_6H_{11}O_5}_{\textit{Maltose}} \\
\quad \downarrow + HOH \\
\underset{\alpha\ \textit{Achroodextrin}}{(C_6H_{10}O_5 \cdot C_6H_{10}O_5)_{7}} + \underbrace{C_6H_{11}O_6 \cdot C_6H_{11}O_5}_{\textit{Maltose}} \\
\quad \downarrow + HOH \\
\underset{\beta\ \textit{Achroodextrin}}{(C_6H_{10}O_5 \cdot C_6H_{10}O_5)_{6}} + \underbrace{C_6H_{11}O_6 \cdot C_6H_{11}O_5}_{\textit{Maltose}}
\end{array}
$$

[4] A. P. Mathews, *Physiological Chemistry*, Wm. Wood & Co., 1930, p. 339.

A limited amount of evidence as to these reactions can be ascertained by anyone by the simple means of chewing an unsweetened cracker. The cracker, which is mainly starch, becomes mixed with the saliva and presently a sweet taste becomes evident which is due to the making of a sugar, in this case maltose.

In the laboratory, salivary digestion of starch can be followed in a test tube in which starch is mixed with saliva and favorable conditions for reaction obtained. The sequence of changes can be followed by the use (1) of iodine to detect the starch, erythrodextrin, and achroodextrin sequence and (2) of Fehling's or Benedict's reagent to detect the appearance of a reducing substance, in this case maltose.

Favoring conditions. The salivas of different individuals have been found to vary markedly as to their starch-digesting ability. But very carefully controlled experimental studies have shown that on the whole, regardless of the source of the saliva, there are certain conditions which favor the functioning of *ptyalin* in speeding up the salivary digestive reactions. These conditions are as follows:

1. Digestion progresses most favorably at a temperature somewhat above body temperature, hence the reactions would appear to be favored by warm food. Cold temperatures, such as those of ice water, inhibit but do not destroy the action of ptyalin, but it is destroyed very quickly at 100° C., and probably at temperatures considerably below this.

2. The favorable hydrogen ion concentration for salivary digestion is slightly on the acid side, at about cH 10^{-6} (pH 6). Digestion, however, can proceed in a basic environment down to one in which cH is 10^{-9} (pH 9), but with continually decreasing activity of the ptyalin; and this enzyme is destroyed in an acid environment of cH 10^{-3} (pH 3). It is significant that this optimum cH of 10^{-6} is slightly more acid than the hydrogen ion concentration of whole saliva and suggests that the most favorable conditions for salivary digestion are met with, not in the mouth, but in the stomach, in which location starch digestion continues until the activity of ptyalin is finally destroyed by the too high concentration of hydrogen ions provided by hydrochloric acid.

Hydrogen ion concentration range in which ptyalin functions

Inactive in environment more basic than	cH 10^{-9}
Optimum environment for activity	cH 10^{-6}
Activity inhibited at about	cH 10^{-5}
Destroyed at about	cH 10^{-3}

3. Salivary digestion of starch seems to be favored by the presence of potassium, carbonate, and phosphate radicals which are provided in the salivary secretion.

4. The functioning of ptyalin decreases continuously with a rising concentration of the products of the reactions which it favors: namely, dextrins and maltose. This is undoubtedly one of the reasons why salivary digestion is not carried forward entirely to the maltose stage, there being no provision for the separation of maltose from the digesting mass.

Continued in the stomach. Following upon the brief mastication period in the mouth the food mass, more or less well mixed with the saliva, enters the stomach. In this location, as has just been mentioned, the reactions involved in salivary digestion may meet with their most favorable hydrogen ion concentration. These reactions take place in the fundus, where there is relatively little mixing with hydrochloric acid, and may continue for some time; but they decrease progressively with the accumulation of products of digestion. Reactions also decrease with increase in the hydrogen ion concentration of the mass and stop entirely when the cH of the digesting mass is such that ptyalin is destroyed.

Gastric digestion. It is a comparatively simple matter to secure supplies of saliva for making a first-hand investigation of salivary digestion; but the investigator who wishes to study the processes of gastric digestion is confronted with a much more difficult problem. One method used for the collection of gastric secretion for such purposes is by means of a stomach tube, but the process is often quite uncomfortable for the subject and specimens of gastric juice obtained are always already mixed with food particles. Direct observations of what goes on in the stomach of the human animal is possible only in cases in which, due to some accident, an opening leading into the stomach permits of first-hand examination; with dogs and other animals such openings are sometimes made purposely; but in either case conditions are not entirely normal. Early workers in the field devised some very original and interesting methods for securing gastric secretions for purposes of experimentation.[5] The first studies of gastric digestion were made about 1822 by Dr. William Beaumont, an army surgeon stationed on Mackinac Island at the head of Lake Michigan. It happened that he was called to give aid to Alexis St. Martin, a Canadian woodsman, who had received a gunshot wound in the abdomen. This wound healed, leaving a permanent fistula opening into the stomach. Dr. Beaumont, recognizing this opportunity to make first-hand studies of the stomach and the processes of gastric

[5] For a summary of early methods used in collecting gastric juice for study, also for a very interesting account of Dr. Beaumont's work in this connection, the student is referred to the account given by Mathews. A. P. Mathews, *Physiological Chemistry*, 1930, pp. 350–356.

digestion, hired St. Martin to submit to such studies. In spite of his isolation, crude equipment, and an uncooperative subject, Dr. Beaumont did a remarkable piece of work which is regarded as a classic in the field of physiological chemistry. Another classic study which added much to the information concerning gastric digestion was that of Pavlov working with dogs as experimental subjects.

Gastric juice. The digestive secretion of the stomach, known as gastric juice, is made by glands located in the inner lining of the stomach called the gastric mucosa. It is believed to be secreted in small amounts continuously, but in greatly augmented quantities with the intake of food. This increased flow of gastric juice is stimulated at first by psychic factors, as in the case of saliva, and later by the entrance of food into the stomach. The latter increase is attributed to the action of a substance called *gastrin* [6] or gastric secretin which, in response to a stimulation induced by the entrance of food into the stomach, is made in certain cells of the mucosa of the stomach and duodenum and is then distributed by the blood to the gastric secretory cells where it stimulates them to action.

Components of gastric juice. It has been found that the normal individual on an ordinary diet secretes from two to three liters of gastric juice daily. The secretion is largely *water*, but other components of major physiological importance are *hydrochloric acid* and digestive enzymes. These enzymes are *pepsin*, which catalyzes the first hydrolysis reactions of proteins, *rennin* which catalyzes the clotting of milk casein, and *gastric lipase* which speeds the hydrolysis of emulsified fats.

Hydrochloric acid, which is secreted by specific glands in the gastric mucosa, seems to be essential to the activity of pepsin. One theory claims that the glands secrete not pepsin but an inactive substance, known as pepsinogen, which on entrance into the stomach in some way reacts with hydrochloric acid in the gastric juice to make the active pepsin. But more recently the theory has been advanced that the change from inactive to active pepsin may be due merely to obtaining the relatively high concentration of hydrogen ions that is essential for pepsin functioning (p. 447) which is made possible through the agency of this strong acid.

[6] According to recent reports *gastrin* may be identical with histamine, a substance closely related to the amino acid histidine. It has been known for some time that the subcutaneous injection of histamine is followed by increased gastric secretion and this compound has been employed for this purpose both experimentally and clinically. See the reports of Ivy and associates, *American Journal of Physiology*, **101**, 331 (1932) and **105**, 220 (1933).

Another fortunate but incidental effect of hydrochloric acid in the gastric juice is that the high concentration of hydrogen ions provided thereby is unfavorable to bacterial growth, consequently many of the bacteria which enter the stomach with the food mass are either inhibited in their growth or actually killed.

The quantity of *hydrochloric acid* secreted varies so markedly from the normal in certain pathological conditions that it is helpful in diagnosis. In carcinoma of the stomach or duodenum, also in certain types of anemia, there may be a marked diminution of hydrochloric acid, a condition called hypoacidity; whereas gastric ulcer and certain neurotic conditions are frequently associated with hyperacidity.

Questions which have long been of interest to physiologists and which have greatly puzzled them are how this strong acid can be secreted from a blood stream which is always basic in reaction, and how it can be made in the cells without destroying the cells which produce it. Various theories have been advanced but the real answer is yet unknown. Certain it is that this acid is present in the stomach and that the normal gastric mucosa is not attacked by it, although there is evidence to indicate that if the gastric mucosa is injured there may be such an attack. It certainly is not stored in the cells of the gastric mucosa but seems to be *made immediately before it enters* the stomach. One theory suggests that it may be made in the lumen of the secreting cells, perhaps from sodium chloride and other substances normally present in the blood stream, and emptied into the stomach itself as rapidly as made. The following equations suggest two such possible reactions:

$$\underbrace{\begin{matrix} H_2CO_3 + NaCl \\ NaH_2PO_4 + NaCl \end{matrix}}_{\substack{\text{Normally present}\\ \text{in the blood stream}}} \begin{matrix}\longrightarrow \\ \longrightarrow\end{matrix} \underset{\substack{\downarrow \\ \text{Secreted}\\ \text{directly}\\ \text{into the}\\ \text{stomach}}}{\begin{matrix} HCl \\ HCl \end{matrix}} \begin{matrix} + \\ + \end{matrix} \underbrace{\begin{matrix} NaHCO_3 \\ Na_2HPO_4 \end{matrix}}_{\substack{\text{Reabsorbed}\\ \text{into the}\\ \text{blood stream}}}$$

If either of these reactions does occur, then it should follow that, during the period when hydrochloric acid is being secreted into the stomach most copiously, there would be an accompanying increase in the blood of either sodium bicarbonate or disodium phosphate; in which event, through the hydrolysis of either salt to make sodium hydroxide, the reaction of the blood would shift temporarily more to the basic extreme of the normal cH range. And as a matter of fact evidence has been obtained that the blood *does* become more basic during active gastric secretion. This evidence is provided in the finding that the intake of food is often followed very soon by a change in the reaction of the urine from an acid condition, which is usual for this excretion, to basic. This indicates that the body has been setting into action one of its mechanisms, by which it prevents the hydroxide ion concentration of the blood from becoming too great. This increase in the hydroxide ion concentration of the blood and urine is referred to as the "alkaline tide."

Chemical reactions as to proteins. The most important reactions in the stomach involve proteins. Under the catalytic influence of *pepsin* proteins react with water to make proteoses and peptones:

$$\text{Proteins} + \text{Water} \xrightarrow{\text{pepsin}} \text{Proteoses} + \text{Peptones}$$

It is believed that the reaction is hydrolytic in nature and that the attack is at the amino-carboxyl linkage (Fig. 92) of the protein molecule. (See also p. 423.)

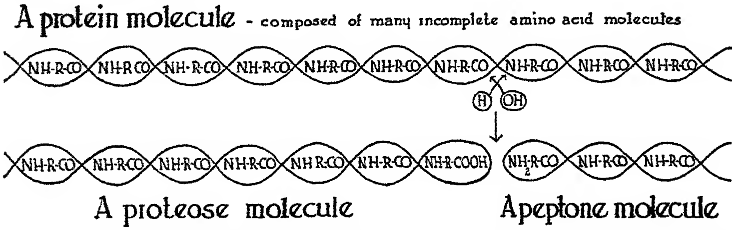


FIG. 92. A Diagram Representation of a Portion of a Protein Molecule, Showing the Nature of the Hydrolytic Attack

Another digestive process which takes place in the stomach is the clotting of the casein of milk. This action is believed to be catalyzed by an enzyme called *rennin* which is made in the glands of the stomach and which is most active in the stomachs of young animals, whose chief natural food is milk. Herein is explained the practice of ancient times of introducing ground portions of the mucosa of a calf's stomach into milk in order to obtain the clotting necessary for the making of one variety of cheese. The exact nature of the reactions concerned is unknown but the following are suggested as the possible steps involved:

$$\underset{\text{(soluble protein)}}{\text{Caseinogen}} + \text{Water} \xrightarrow{\text{rennin}} \underset{\text{(soluble protein)}}{\text{Casein}^{7}}$$

$$\text{Casein} + \text{Calcium salts} \longrightarrow \underset{\text{(an insoluble protein salt)}}{\text{Calcium caseinate}}$$

The student may wonder what possible advantage there can be to the young animal in having an insoluble protein made in the stomach. Mathews [8] suggests that the reason may be that whereas milk would quickly pass through the stomach to the intestine, the semisolid curds made by clotting are delayed, thus providing for a longer exposure of milk protein to the proteolytic enzyme in the stomach.

[7] According to another nomenclature, which is frequently met with in reading, the names used for these substances are casein (for caseinogen), paracasein (for casein), and calcium paracaseinate.

[8] A. P. Mathews, *Physiological Chemistry*, 1930, p. 394.

Favoring conditions. Certain conditions which favor the reactions concerned with the digestion of proteins have already received some attention. (1) The large surface of contact between proteins and gastric juice is provided for by the spreading-out effect of the considerable quantity of water secreted and by mixing due to muscular movements of the stomach. (2) The hydrogen ion concentration range in which pepsin functions at its optimum for speedy protein hydrolysis is another important factor. This optimum cH for pepsin activity varies somewhat with different proteins but always lies within the comparatively high range of from cH $10^{-1.2}$ to $10^{-3.5}$ (p. 260):

Pepsin most active	cH $10^{-1.2}$ to $10^{-3.5}$
Pepsin destroyed	cH 10^{-4}

(3) The time element of from two to seven hours that the food mass remains continually in contact with the gastric juice — although in decreasing quantities as portions are passed on to the intestine — is another factor which favors gastric digestion of proteins. *An inhibiting factor* as to the progress of gastric digestion is the increasing quantity of proteoses and peptones which are made as digestion progresses.

Gastric digestion of fats. Whether or not the digestion of fats takes place at all in the stomach was long a debated question. But it is now generally agreed that there is such digestion but only on the part of fats which are already emulsified such as glyceryl butyrate and other fats of butter and egg yolk. The catalyst provided for speeding up the reactions involved is known as *gastric lipase* and the reaction is believed to be that of hydrolysis:

$$\begin{array}{llll} \text{Fats (emulsified)} + \text{Water} & \xrightarrow{\text{gastric lipase}} & \text{Fatty acids} & + \text{Glycerol} \\ C_3H_5(C_3H_7COO)_3 + 3\,HOH & \longrightarrow & 3\,C_3H_7COOH & + C_3H_5(OH)_3 \\ \text{Glyceryl butyrate} & & \text{Butyric acid} & \quad\text{Glycerol} \end{array}$$

Gastric digestion of carbohydrates. No enzyme is provided in the gastric juice to catalyze the digestion of carbohydrates. It is probable that the only carbohydrate digestion that takes place in the stomach is the previously mentioned continuation of salivary digestion of starch which is catalyzed by ptyalin in the less acid portions of the gastric food mass.

Gastric digestion continues in the intestine. The semifluid digesting mass on its entrance through the pyloric valve into the duodenal part of the intestine is strongly acid in reaction due to the hydrochloric acid present. In this location, however, as the acidic

advancing mass comes in contact with the basic secretions from the glands of the pancreas, liver, and intestine, its hydrogen ion concentration is decreased. But there is reason for believing that at times this is a very gradual process; as a result, it is reasonable to conclude that the peptic hydrolysis of proteins should be able to continue in the more acid regions within the intestine at decreasing speed with decreasing hydrogen ion concentration until the environment reaches a cH of about 10^{-4}, when the pepsin is destroyed.

Intestinal digestion. The difficulties which the investigator encounters in attempts to obtain information concerning intestinal digestion are even greater than with gastric digestion. As with gastric digestion he is dependent for most of his data upon observations that attend surgical entrance into the intestine, and digestion under such conditions may not be normal. And aside from the intestine, two glands, the pancreas and the liver, are involved. Furthermore, the great length of the intestine itself complicates the problem, since digestive phenomena observed in one part of the intestine may differ from those in other parts of this lengthy organ. But despite difficulties, some facts have been gleaned from such observations and experimental studies as have been possible and some reasonable theories have been developed which seemingly fit in with the facts. The consideration of these factual findings and some of these beliefs constitute our next study.

The digestive secretions. The partially digested, semifluid material which passes from the pylorus of the stomach to the duodenum is known as chyme. The entrance of this acid chyme into the duodenum stimulates the secreting glands of the intestinal mucosa, as the result of which a fluid, known as intestinal juice (or succus entericus), is poured into the intestine. The acid chyme also stimulates the secretion within the intestinal mucosa of a hormone, called *secretin*, which is absorbed by the blood stream, carried to the pancreas, and causes it, in turn, to secrete pancreatic juice. This secretion flows through the pancreatic duct and empties into the duodenum about five inches below the pyloric valve. Bile, which is made in the liver, likewise enters the duodenum through the duct which serves for the entrance of both pancreatic juice and bile (Fig. 93). The major component, as to quantity, of these three secretions — the intestinal juice, pancreatic juice, and bile — is *water*, but they also contain certain enzymes and other substances which function importantly in carrying the digestive processes to completion.

The ***pancreatic secretion*** provides a number of digestive enzymes of which the most important are: (1) *trypsinogen* the precursor of trypsin, (2) *steapsin* or pancreatic lipase for catalyzing the hydrolysis of fats in the intestine, and (3) *amylopsin* or pancreatic amylase, a catalyst for the hydrolysis of starches and dextrins.[9]

The ***intestinal secretion.*** The intestinal secretory glands are in the intestinal mucosa and are distributed throughout the entire small intestine, but they are especially concentrated in the duodenum and upper regions of the intestine. The secretion provided contains another group of digestive enzymes: (1) *enterokinase* activates trypsinogen to make active *trypsin,* which speeds up the hydrolysis of proteins, proteoses, and peptones; (2) *erepsin*[10] aids in the hydrolysis of peptids to make amino acids; (3) a *maltase,* a *sucrase* and a *lactase* catalyze the hydrolysis of the disaccharids maltose, sucrose, and lactose respectively. As for lactase it is of interest to note that although it is commonly present in the digestive juice of children and in the young of animals whose food is largely milk, it is less frequently encountered in the

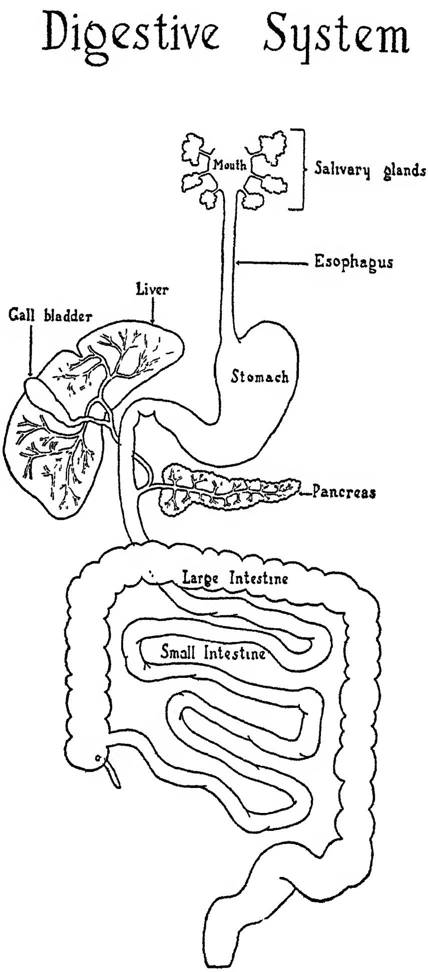


FIG. 93

[9] Another proteolytic enzyme called carboxy polypeptidase has recently been reported to be present in pancreatic secretion which catalyzes the hydrolysis of polypeptids to make simpler peptids and amino acids. Other enzymes reported in this secretion are a maltase, a sucrase, and a lactase, the last mentioned only in the young animal.

[10] Erepsin is reported as being really a mixture of enzymes including polypeptidases, di and tri peptidases.

digestive juice of adults in whose diet milk plays a less important part.

Bile is made in the liver and between periods of digestion is stored in the gall bladder. As digestion sets in bile flows into the duodenum by way of the common bile and pancreatic juice duct. Unlike the pancreatic juice, bile contains substances for excretion as well as substances which aid digestion in the intestine. This is because, unlike the pancreas, the liver is an excretory as well as a secretory organ. Bile components vary somewhat in different animals, but the following substances are fairly common to all:

Bile

Secreted as aids in digestion	*For elimination*
Water	Bile pigments
Sodium bicarbonate	Bilirubin (red)
Bile salts	Biliverdin (green)
Sodium glycocholate	Cholesterol
Sodium taurocholate	(also a digestive aid)

It is important to note that in contrast with all other digestive juices bile contains no enzymes. The *water* provided functions, of course, as does the water from other secretions and from the food mass: from a physical angle it helps to spread out the digesting food mass, and chemically it is itself involved in the digestive reactions. *Bile salts* together with *cholesterol* function as emulsifying agents for fats. This necessary substitute for solution — fats being subject to neither true nor colloidal solution — is of exceeding digestive importance in two ways: (1) it removes fat coatings around bits of carbohydrate and protein, thus rendering these substances available for digestion; (2) it effects the distribution of fats as fine globules, thereby submitting them to a larger area of contact with digestive juices, hence with the fat digesting enzyme steapsin. *Bile salts,* also, aid in a way not well understood in the absorption of the fatty acid end products of digestion, one theory being that they increase the permeability of the cell membranes.

It is known that when, due to some obstruction, bile fails to enter the intestine, the digestion of fats is greatly interfered with, consequently to a less extent that of carbohydrates and proteins; and fatty material is excreted in the feces.

Substances for elimination. Cholesterol, a vitally essential and widely distributed substance in body cells, finds its way out of the body through the liver. Despite its importance it would seem to be a difficult substance for the

body to cope with because of its very slight solubility in all body fluids. *Bile* salts, however, render aid in keeping normal quantities of cholesterol in suspension in the bile, thus preventing the precipitation of this difficultly soluble compound in the gall bladder and bile ducts and providing for its elimination into the intestine and on out of the body with the feces. But when cholesterol, for any reason, accumulates in the bile in higher concentration than normal it does precipitate in the gall bladder or bile ducts and may gather in the troublesome accretions known as gallstones.

The *bile pigments,* bilirubin and biliverdin, are made from the hemoglobin of worn-out red blood cells and are emptied with the bile into the intestinal tract for elimination; they are responsible to a considerable extent for the characteristic color of feces. When, due to some obstruction such as the above mentioned gallstones, the passage of bile into the intestine is interfered with, these pigments get into the blood stream and give rise to the skin coloring associated with jaundice.

Chemical digestion in the intestine. The food mass (now called the chyme), as it enters the intestine from the stomach, contains substances of protein, fat, and carbohydrate nature as follows:

Protein in nature	*Of fat origin*	*Carbohydrates*
Undigested proteins	Undigested fats	Glucose
Proteoses	Glycerol } in small	Fructose
Peptones	Fatty acids } amounts	Sucrose
Nucleoproteins		Maltose
		Lactose
		Undigested starches
		Dextrins
		Celluloses

The small amounts of glycerol, fatty acids, glucose, and fructose which are present are ready for absorption. Nucleoproteins are very complex compounds and little information is available as to the digestive sequence to which they are subjected. There is no provision for hydrolysis of celluloses in humans. All other substances mentioned are subject to digestive reactions. These reactions, and the favoring conditions that must be obtained in order to enable the enzymes to continue their catalytic activity until their respective reactions are carried to completion, are the next subjects for consideration.

Reactions involving proteins. Reactions of the remaining proteins and of proteoses and peptones with water to make peptids are speeded up all along the small intestine through the agency of the powerful enzyme trypsin; and the peptids, in turn, are hydrolyzed to make the digestive end products amino acids, the reactions being catalyzed by erepsin (a peptidase or mixture of peptidases):

$$\left.\begin{array}{l}\text{Proteins}\\ \text{Proteoses}\\ \text{Peptones}\end{array}\right\} + \text{Water} \xrightarrow{\text{trypsin}} \text{Peptids}$$

$$\text{Peptids} + \text{Water} \xrightarrow{\text{erepsin}} \text{Amino acids}$$

All of these hydrolysis attacks are believed to take place at amino-carboxyl linkages in the various molecules after the manner presented on page 423.

The findings of various investigators indicate that a somewhat basic environment is most favorable to the catalytic functioning of both trypsin and erepsin. Trypsin is reported to be most active at from about pH 8 to 11,[11] and erepsin from about pH 7 to 8.[12]

Reactions involving fats. Save for the very small portions of already emulsified fats which have been hydrolyzed by gastric lipase, all fats reach the intestine just as they were on the plate, save that they have been severed into smaller bits by the mechanical motions of the stomach. In the intestine, however, they meet with provision for their emulsification (p. 450), and with the very efficient enzyme steapsin, for speeding up their hydrolysis to make fatty acids and glycerol:

$$\text{Fats} + \text{Water} \xrightarrow{\text{steapsin}} \text{Glycerol} + \text{Fatty acids}$$

The fats which are commonly present in the ordinary diet are stearin, palmitin, olein, and butyrin and the reactions involved in their digestion are all after the manner of that on the part of stearin as represented in the following equation:

$$\begin{array}{ccccc}\text{Stearin} & + \ \text{Water} & \xrightarrow{\text{steapsin}} & \text{Glycerol} & + \ \text{Stearic acid}\\ C_3H_5(C_{17}H_{35}COO)_3 & + \ 3\ HOH & \longrightarrow & C_3H_5(OH)_3 & + \ 3\ C_{17}H_{35}COOH\end{array}$$

The reaction environment most favorable to the activity of steapsin appears to be about neutral (pH 7).

Reactions involving carbohydrates. The carbohydrates that enter the intestine with the food mass include any small quantities of glucose, fructose, sucrose, and lactose which may have been provided in the diet; starches which have escaped salivary digestion; and dextrins, maltose, and celluloses. In the presence of the enzyme amylopsin (pancreatic amylase) the starches and dextrins react with water to make maltose. Maltose, sucrose, and lactose, in the presence of the enzymes maltase, sucrase, and lactase respectively, are hydrolyzed to make glucose, fructose, and galactose.

[11] Northrop's findings as reported by Bodansky, *Introduction to Physiological Chemistry*, 1938, p. 147.

[12] P. B. Hawk and O. Bergeim, *Practical Physiological Chemistry*, P. Blakiston's Sons & Company, 1931, p. 317.

(See p. 352 for an equation representing such reactions.) These reactions probably progress most favorably in a hydrogen ion concentration about neutral, the reported optimum for amylopsin functioning being about pH 7–7.2, for intestinal sucrase about pH 7.[13] The end products of carbohydrate digestion are glucose (predominantly), fructose, and galactose.

Celluloses do not undergo hydrolysis in the intestine of the human; and save for some attack by bacteria, chiefly in the large intestine, they are eliminated as celluloses in the feces. They do, however, play an important part in digestion in that they provide bulk for the intestinal contents, which is one of the peristalsis-promoting factors.

Favoring conditions for completion of digestion. Various conditions for the favoring of the several digestive reactions in the intestine have already received more or less attention in the foregoing discussion, but they merit a final summary presentation. But in this connection it is important to call to mind the fact that it is only in the intestine that these reactions are able to move forward continuously to approximate completion; and the reason for this is that only in the intestine is provision made for the absorption of by far the major portion of the substances that comprise the digestive end products. This provision is also considered further in the following summary.

1. *Favoring enzymes.* Foremost among essentials for the favoring of digestive reactions in the intestine, as is true of the salivary and gastric digestive reactions, is the aid rendered by the respective enzymes.

2. *Large surface of contact.* Another favoring condition is the remarkable provision that nature has established for bringing reacting food substances into contact with water and with enzymes: (a) by means of the considerable intestinal area due both to the length of the intestine, and to the villi of the intestinal mucosa whose secreting cells pour the digestive juice into the food mass all along the way; (b) by means of unceasing mixing accomplished by muscular movements of the intestine during all the hours that the food mass remains in this region; and (c) by means of the spreading-out that is obtained through the ability of disaccharids to make true solutions; of albumins, globulins, proteoses, peptones, and peptids to make colloidal solutions; and of fats to make emulsions with the help of cholesterol, bile salts, and soluble proteins.[14]

[13] H. C. Sherman, *Chemistry of Food and Nutrition*, 1941, p. 83.
[14] A. W. Thomas, *Colloid Chemistry*, McGraw-Hill Book Company, 1934, p. 426.

3. *Favoring hydrogen ion and hydroxyl ion concentrations.* The hydrogen (and hydroxyl) ion concentration is another essential digestive factor of importance; this has already received some attention. All three of the secretions provided — pancreatic juice, intestinal juice, and bile — are more or less basic. The component provided by these secretions which is, in the main, indirectly responsible for this basic reaction is *sodium bicarbonate,* which hydrolyzes to make the strong base sodium hydroxide, and weak carbonic acid. Probably it is the alkalinity of these intestinal digestive juices in themselves that led for so long to the assumption that from duodenal regions on the intestinal contents are alkaline. This is now known to be in error. For while it is true that sodium bicarbonate of these secretions does indirectly provide hydroxyl ions (p. 494), nonetheless, there are several opposing sources of hydrogen ions; these include not only hydrochloric acid but fatty acids and amino acids as products of digestion all along the small intestine.

Consequently, while in parts of the intestinal tract the reaction of the contents is slightly acid and in other parts slightly basic, in most regions, according to observations drawn from recent research, the hydrogen-hydroxyl ion concentration of the intestinal food mass appears to be maintained, for the most part slightly on the acid side, with hydroxyl ions prevailing at times in some locations, more especially in peripheral regions. But this variation from neutral, to slightly acid, to slightly basic makes it certain that sooner or later each enzyme will encounter the cH environment which is optimum for its activity in speeding up the digestive reaction in respect to which it functions. Hydrogen ion optimums as reported for some of the digestive enzymes have already been given from time to time in their appropriate connections, and they are stressed again in the accompanying summary (p. 455).

4. *Time.* The length of time of from about six to twelve hours that it normally requires for the food material to pass through the small intestine is another important digestive factor, since opportunity is thereby provided for long periods of contact of the substances subject to digestion with water and with their favoring enzymes.

5. *Provision for absorption.* Lastly we come to absorption, which is really the final factor that determines whether or not all of the proteins, carbohydrates, fats, and intermediate products are finally able to meet with their digestive fates; since it is only upon removal of the products of reaction (p. 440) which an enzyme catalyzes, that it can continue to function until all of the food substance concerned is hydrolyzed; and it is *only* in the intes-

tine, where ample provision is made for the removal of end products, that this is possible. Only with the continuous removal of amino acids by absorption (see below) can trypsin and erepsin carry the hydrolysis of proteins, proteoses, peptones, and peptids forward until none of these food substances is left in the intestine; only with the continuous removal of glucose by absorption can amylopsin and maltase carry the hydrolysis of starches, dextrins, and maltose to completion. Similarly, the enzymes sucrase, lactase, and steapsin are able to catalyze the respective hydrolyses of all the sucrose, lactose, and fats left in the intestine only upon the continuous absorption of glucose, fructose, and galactose into the blood, and of fatty acids and glycerol into the lacteals.

In the intestine				*Absorbed*
Proteins, Proteoses, Peptones + Water	$\xrightarrow[\text{pH 8}]{\text{trypsin}}$	Peptids + Water $\xrightarrow[\text{pH 7.7}]{\text{erepsin}}$ Amino acids	$\longrightarrow$	Blood
Starches, Dextrins + Water	$\xrightarrow[\text{pH 7.0}]{\text{amylopsin}}$	Maltose + Water $\xrightarrow[\text{pH 6.7–7.2}]{\text{maltase}}$ Glucose	$\longrightarrow$	Blood
Sucrose + Water	$\xrightarrow[\text{pH 6.8}]{\text{sucrase}}$	Glucose	$\longrightarrow$	Blood
		+ Fructose	$\longrightarrow$	Blood
Lactose + Water	$\xrightarrow{\text{lactase}}$	Glucose	$\longrightarrow$	Blood
		+ Galactose	$\longrightarrow$	Blood
Fats + Water	$\xrightarrow[\text{pH 7.1–7.9}]{\text{steapsin}}$	Glycerol	$\longrightarrow$	Lymph
		+ Fatty acids	$\longrightarrow$	Lymph

Under normal conditions it is probable that, of the digestive products of protein origin, only the amino acid end products can pass through the intestinal membrane. There is reason to believe, however, that under some conditions this membrane may be permeable to polypeptids and perhaps even to peptones or proteoses. This is of interest because it is thought by some to explain the marked hypersensitiveness shown by some people, especially by some infants, to certain proteins of the food mass. This hypersensitivity is usually evidenced shortly after the protein in egg, fish, or other food source has been eaten.

There is much that is yet unknown concerning the mechanism of intestinal absorption. But two favoring conditions that have received some consideration previously are: the great area of contact as to the digestive end products with the absorbing membranes (p. 453), and the provision through alternate muscular movements for carrying away blood laden with these products and for bringing in fresh blood supplies (p. 437). Probably the ability of some substances to get into true solution, thereby rendering them subject to diffusion through the intestinal membrane is another factor; but it is known that absorption of water-soluble substances is actually carried on more rapidly than can be accounted for on this basis only. It is also known that bile salts aid in the absorption of fatty acids, but the process by which this is accomplished is still a mystery.

Proportion of compounds digested. Almost all, if not all, digestive reactions end in the small intestine, and absorption is practically completed in this region; some absorption can seemingly occur from the large intestine, notably as to water, glucose, and products of bacterial action. And so ample has been the provision for digestion that, with normal alimentary functioning, surprisingly small proportions of carbohydrates, fats, and proteins previously on the plate, and of their hydrolysis products, get carried on into the large intestine with the undigested residue. According to Sherman[15] the following figures are approximate averages:

	End products of digestion absorbed	*Undigested portions and end products not absorbed*
Carbohydrates	98%	2%
Fats	95%	5%
Proteins	92%	8%

Bacterial action in the large intestine. A surprising amount of bacterial action takes place in the intestine normally, the chief location of these activities being in the large intestine. Although the intestinal tract of the newborn infant is practically free from these microörganisms, probably within twenty-four hours they have begun to accumulate and multiply enormously. From then

[15] H. C. Sherman, *Chemistry of Food and Nutrition*, 1941, p. 128.

on, during the entire life of the individual, bacteria are inhabitants of the intestine. Under normal conditions few living bacteria are present in the food mass as it leaves the stomach, nor are they abundant in the small intestine; but the number and variety found in the large intestine is almost unbelievable. Indeed, more than one-fourth of the solid material of the feces is made up of bacteria, living or dead. Many of these organisms are nonpathogenic but pathogens are found there as well. However, our present concern is less with the varieties of microörganisms present than with some of the chemical changes which food substances may undergo as a result of the activities of these organisms. Concerning these changes little is really known but certain items are quite generally agreed upon. Some of these are presented in the following.

On carbohydrates. The carbohydrates which undergo chemical changes due to bacterial action are for the most part the otherwise indigestible celluloses present in the large intestine. The products that result from these reactions are chiefly gaseous substances and organic acids, some of which are as follows:

$$\left.\begin{array}{l}\text{Hydrogen}\\ \text{Methane}\\ \text{Carbon dioxide}\end{array}\right\}\text{not absorbed but eliminated from the intestine.}$$

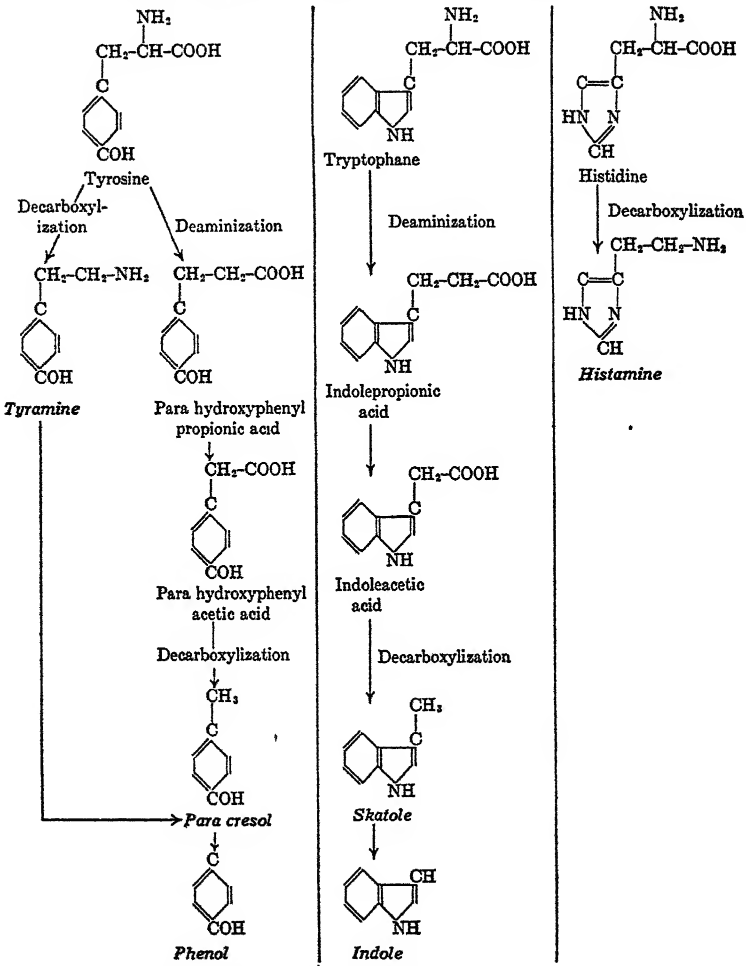
$$\left.\begin{array}{l}\text{Acetic acid}\\ \text{Butyric acid}\\ \text{Lactic acid}\end{array}\right\}\text{absorbed and distributed to the cells.}$$

When made in normal quantities these products are responsible for no ill effects. But if peristalsis is sluggish, the carbohydrates impregnated with bacteria will remain in the large intestine for a longer than normal period; in which event the accumulated gases give rise to considerable discomfort, and some of the other products in these higher than normal concentrations are irritating and may cause diarrhea.

On fats. A certain amount of fat hydrolysis takes place in the large intestine to make fatty acids and glycerol, possibly through the agency of enzymes within the bacteria. Other than this little is known or conjectured in regard to bacterial action on fats or their digestive products.

On amino acids. Any proteins that are present in the large intestine are subject to bacterial attack to make proteoses, peptones, amino acids, hydrogen sulfide, and ammonia. But the most important bacterial actions on substances of protein origin are those in respect to amino acids. These acids undergo two varieties of attack: (1) a decarboxylization, meaning the making of carbon dioxide from the carboxyl of the amino acid; (2) a

deaminization followed by decarboxylization. The accompanying table represents some of the most important compounds made in such manner from *tyrosine, tryptophane, and histidine.*



These substances are in part absorbed and eliminated in the urine, either unchanged or somewhat altered, and in part carried out in the feces. A number of human ills which are associated with constipation — such as headache, drowsiness, insomnia, irritability, skin eruptions, etc. — have for long been attributed to the absorption of some of these substances, especially *indole* and *skatole*, also to a lesser extent *cresol* and *phenol.* These claims may possibly hold when excessive quantities of these compounds

are absorbed, but there is no experimental evidence to support the claims; and certain it is that nature provides for the detoxification of these substances in normal quantities through what is called conjugation, which involves reaction with sulfuric acid and potassium salts. The end product of this conjugation with indole is indican, which is eliminated in the urine.

Tyramine and *histamine* are very toxic when administered either intravenously or intramuscularly, but when absorbed from the intestine provision is made by nature for their detoxification, tyramine in the liver and histamine possibly in the intestinal membrane and other organs.

Composition of feces. When the processes of digestion, bacterial action, and absorption are complete, any remaining food mass together with certain materials picked up from secretions entering the intestinal tract are eliminated as feces. In this mass are present:

Water	In variable amounts
Celluloses	Nearly all ingested.
Undigested carbohydrates and their digestive products	2%
Undigested fats, fatty acids and glycerol	5% approximately, of the quantity taken in from the mass on the plate.
Undigested proteins and their digestive products	8%
Skatole, indole, and other products of bacterial action on amino acids	Largely responsible for the odor of feces.
Salts:	
Calcium salts	The greater part of the calcium salts eliminated in the course of metabolism find their exit through the intestine in the feces.
Salts of heavy metals	Copper, lead, and iron salts.
Bile pigments: Bilirubin Biliverdin	Made from hemoglobin of worn-out red blood cells and largely responsible for the color of the feces.
Cholesterol	Eliminated through the liver, finds exit in the feces.
Various gases: Methane Hydrogen Carbon dioxide	From bacterial action on carbohydrates in the large intestine.
Hydrogen sulfide	From cystine and methionine by bacterial action.
Bacteria — dead and living	Comprise from one-quarter to one-half of the bulk of the solid matter of feces.

Questions

1. What is digestion? Why is it essential for most components of the food mass to undergo this process?

2. What, if any, components of the food mass can be absorbed without undergoing digestion? Give reason.

3. Explain how the various physical processes along the digestive tract function as aids to the chemical processes of digestion.

4. What is an enzyme? What, in general, is the function of the digestive enzymes?

5. Why are the digestive reactions classed as hydrolytic in nature? Illustrate through the use of suitable formula equations for the reactions concerned in the hydrolysis of a disaccharid, a starch, a fat, and a tripeptid.

6. What digestive secretions are provided along the alimentary tract? Where is each secreted? What are the major components of each secretion? What, if any, function has each component in relation to the digestive reactions?

7. What provisions have been made by nature for obtaining the various hydrogen ion concentrations that are favorable to the activities of the different digestive enzymes?

8. Prepare a summary chart which will contain the following information regarding the digestive reactions:
   a. Locations along the digestive tract where reactions occur and the average time spent by the food mass in each region.
   b. Word equations for the reactions occurring in each region, indicating the functioning enzyme and the cH environment favorable to the activity of each specific enzyme.
   c. The end products of digestion and the path of removal of each product from the digestive tract.

9. What provision is made for the emulsification of fats? Give two reasons why emulsification is important for normal digestion.

10. What is the digestive functioning of the celluloses of the food mass? What finally happens to them?

11. What substances are made in the intestinal tract as the result of bacterial activity? What happens to these substances?

12. What effect might each of the following conditions have upon the digestive process as a whole: (a) the bolting of food, (b) sluggish peristalsis, (c) hyperactive motility along the intestinal tract, (d) constipation, (e) obstruction of the bile duct, (f) excessive use of sodium bicarbonate or other base-forming compound, especially shortly before meals?

CHAPTER XXX

Function and Fate of Glucose, Fats, and Proteins in the Body

The scientist who attempts to learn the nature of the reactions which are constantly in progress within living cells and attempts to wrest from nature the secrets as to cell functionings encounters great difficulties in his studies. Much of the information acquired must be based upon what can be learned from the study of cells from freshly killed animals; and no matter how swiftly the work may be done some changes have already taken place; although just what changes may occur in that brief interval which marks the boundary between life and death are for the most part unknown. When the scientist has gathered what facts he can there still remain gaps to be filled. These gaps he bridges when possible with the best reasoning guesses which he can devise that fit in with the known facts, but frequently theories and interpretations of facts have to be revised in the light of new discoveries. Consequently, in any attempt to study the chemical reactions which go on within living cells we are entering a field in which there are a few well established facts, much that is but partially understood, and a great deal that is as yet unknown.

FUNCTION AND FATE OF GLUCOSE

In the liver. When the blood, laden with products of digestion, is brought from the intestine to the liver, part of the glucose, and perhaps all of the fructose and galactose are removed by the liver cells and used seemingly for the making of glycogen. This is evidenced by the fact that the relative concentration of the sugars in the portal tube, which carries the blood from the intestine to the liver, during the period of absorption is considerably higher than the concentration of the glucose in the hepatic vein leaving the liver, a discovery that was first made by Claude Bernard, a French physiologist, about 1843. The making of glycogen from these

sugars is believed to be a dehydrolysis reaction catalyzed by some enzyme present within liver cells:

$$\left.\begin{array}{l}\text{Glucose}\\ \text{Fructose}\\ \text{Galactose}\end{array}\right\} \rightarrow \text{Water} + \text{Glycogen}$$

$$^{1}\ n\ C_6H_{12}O_6 \longrightarrow n\ HOH + (C_6H_{10}O_5)_n$$

The glycogen thus made, because of its insolubility in water, is incapable of dialyzing through cell membranes and is, therefore, held in storage in the liver cells. But it, in turn, is subject to hydrolysis to make glucose which, being soluble, can pass from liver cells into the blood. In this connection it is interesting to note that whereas it is believed that all three monosaccharids — glucose, fructose, and galactose — are used by the liver for making glycogen, it is known that the only product of glycogen hydrolysis is glucose. It is also known that an enzyme, called glycogenase, is present in liver cells which functions as a catalyst for this latter reaction:

$$\text{Glycogen} + \text{Water} \xrightarrow{\text{glycogenase}} \text{Glucose}$$

$$(C_6H_{10}O_5)_n + n\ HOH \longrightarrow n\ C_6H_{12}O_6$$

The above reactions may not take place in the manner suggested and probably are not as simple as implied. But it is certain that there is some provision in the liver for the transformation of a monosaccharid, or monosaccharids, into glycogen and of glycogen into glucose; it is also certain that liver glycogen — its increased making and storage at times, its depletion to make glucose at other times — is part of the mechanism for maintaining a fairly constant concentration of glucose in the blood for transportation to the active cells. A finding which supports these facts is as follows: after a meal rich in carbohydrate a slight increase in the concentration of blood glucose is always accompanied by a marked increase in the glycogen content of the liver. The obvious conclusion from this finding must be that under such circumstances reactions are favored for the making of glycogen. But when actively functioning cells are drawing upon glucose in the blood to meet their demands, even though such demands may be excessive, as during strenuous exercise, the concentration of glucose in the blood remains quite constant whereas the glycogen store of the liver becomes depleted. Under such circumstances, therefore, one can only conclude that the reaction or reactions in the liver are

[1] From twelve to eighteen glucose units are claimed to combine to make one glycogen unit. Wm. R. Fearson, *An Introduction to Biochemistry*, The C. V. Mosby Company, 1940, p. 96.

being favored whereby glucose is continuously made at the expense of glycogen.

The storage of liver glycogen appears to be favored by the presence of *insulin*, the hormone which is secreted by the islands of Langerhans of the pancreas; but whether this hormone favors the synthesis of glycogen, or whether it functions by inhibiting its hydrolysis, has not been established. The hormone *epinephrine*, produced by the adrenal glands, is antagonistic to insulin in this respect in that it appears to hasten the hydrolysis of glycogen thereby causing glucose to be poured into the blood stream. Advantage is taken of the opposite effects of these two hormones in the treatment of diabetic patients when an abnormally low concentration of glucose in the blood (hypoglycemia) follows upon an overdose of insulin, in which case injections of adrenalin (epinephrine) are sometimes resorted to for bringing about a prompt increase in blood glucose.

The three monosaccharids already mentioned are not the only substances from which the liver cells can make glycogen. Other substances which are used for this purpose are lactic acid, which is an intermediate product of glucose metabolism, glycerol, and certain of the amino acids.

Glucose in the blood. Glucose is the only sugar present in any considerable amount in the blood leaving the liver and it is there only for transportation to functioning cells throughout the various tissues and organs. Normally, the glucose content of blood, commonly referred to as blood sugar, is quite constant, varying from 70 to 90 mg. per 100 cc. of blood. And although during the period of absorption this content may increase to from 120 to 130 mg. per 100 cc. of blood, within about two hours after the meal the blood sugar returns to its usual level. In diabetes the concentration of blood glucose is abnormally high, supposedly due to the inability of the liver to store glycogen and of the cells to make use of glucose in the absence of insulin. An increase in the glucose concentration of the blood above the tolerance of the individual, whether temporary due to a high intake of carbohydrate food, or more or less continuous as in diabetes, results in excretion of glucose by the kidneys, a condition known as glycosuria.

Glucose in the cells with oxygen to provide energy. Probably the outstanding function of the glucose carried to the cells is to provide partner substances for reactions with oxygen to produce energies which are so vitally important for the activities of the cells. Each gram of glucose so used draws into reaction 1.06 grams

of oxygen to make carbon dioxide and water as the final matter products, but during the reaction there is an associated energy transformation which results in an energy product of 3.75 Calories.

$$\begin{array}{ccccccccc} \text{1 gram} & & \text{1.06 grams} & & & & & & \\ C_6H_{12}O_6 & + & 6\,O_2 & \longrightarrow & 6\,CO_2 & + & 6\,H_2O & & \\ \downarrow & & \downarrow & & \downarrow & & \downarrow & & \\ \text{Chemical energy} & + & \text{Chemical energy} & \longrightarrow & \text{Chemical energy} & + & \text{Chemical energy} & + & \textit{3.75 Calories of kinetic energy}\text{, heat, or such other energies as the cells need.} \end{array}$$

The first study of this important function of oxygen was made by Lavoisier in the latter part of the 18th century. He recognized not only the matter products of the reaction, carbon dioxide and water, but also the associated energy products. He did not know where in the body the reactions occur nor did he have any idea as to the various intermediate stages.

When these reactions take place within muscle cells, which make up the great bulk of the tissues, a considerable portion of this energy product must appear as kinetic energy for the contraction of muscles when walking, lifting, etc., for the constant beating of the heart, and for the movements involved in respiration and in peristalsis; then as this work is performed the kinetic energy is transformed into heat. However, there is reason to believe that kinetic energy is not necessarily the only energy made in muscle cells, but that at the same time, some heat is made directly as well as any other energy that may be in demand.[2] Similar matter transformations take place in the cells of the nervous system which are also accompanied by energy transformations during which the special variety of energy or energies are made which are necessary to the peculiar functioning of these cells.

It is a generally accepted belief that glucose obtained within the cells does not react with oxygen directly, as might be inferred from the foregoing equation, but rather that a number of intermediate reactions take place before substances are obtained which do react with oxygen. Just what these intermediate reactions may be is a problem which has engaged the interest and research efforts of biochemists for years and there is much which remains to be learned in regard to this matter. It is our purpose to outline only some of the generally agreed-upon stages in the process as it has been studied in reference to muscle cells.[3]

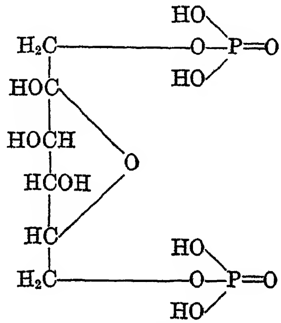
[2] H. C. Sherman, *Chemistry of Food and Nutrition*, The Macmillan Company, 1941, p. 170.

[3] An excellent statement of the problem is to be found in *Introduction to Physiological Chemistry*, by Meyer Bodansky, 1938, pp. 321–322, and a discussion summarizing the results of recent research on this subject is to be found in the succeeding pages.

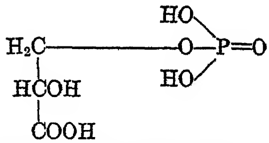
Intermediate metabolism of glucose within muscle cells. Part, if not all, of the glucose which is taken into muscle cells undergoes dehydrolysis to make water and muscle glycogen, a polysaccharid which, like liver glycogen, being colloidal in nature, is retained within the cells. When the muscles need to make energy this muscle glycogen is depleted and lactic acid is made. With adequate oxygen brought to the cells by the blood stream this lactic acid disappears as rapidly as it is made, part presumably being built back into glycogen, and part reacting with oxygen brought to the cells by the hemoglobin to make carbon dioxide and water. It seems probable that it is during this reaction of oxygen with lactic acid that the energy product is made which is indirectly responsible for the work done by the muscle.

Glycogen to lactic acid. Undoubtedly a number of intermediate reactions take place in the making of lactic acid from glycogen, some of them apparently being quite involved. In the early stages of the reaction sequence phosphates are known to play an important role, glycogen apparently engaging in reactions with phosphoric acid by which hexosedihydrogenphosphate esters are made. These hexose phosphates, so-called, are used in turn for the making of a number of compounds which are derivatives of glycerol and phosphoric acid; the final of these derivatives is called phosphoglyceric acid. At this stage the phosphate separates from the compound, and pyruvic acid, believed to be the immediate precursor of

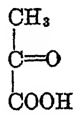
Structural formulas for some of the supposed intermediate products in the glycogen to lactic acid stage of glucose metabolism in muscle cells.



Hexosediphosphate
(Harden-Young ester)



β-phosphoric glyceric acid



Pyruvic acid

Lactic acid

lactic acid, is made and the phosphate itself is again made available for reaction with more glycogen. The pyruvic acid then becomes reduced to make lactic acid. Any reactions within the sequence from glycogen to lactic acid that are oxidative in nature engage oxidizing agents, not oxygen brought by the hemoglobin, and are accompanied by complementary reductions. Therefore, relatively speaking, only a small quantity of energy product for doing the work of the cells is believed to be made until the lactic acid stage is reached.

Immediate source of energy for muscle contraction. The fact seems to be well established that while oxygen substance is, in the final analysis, the major source of energy for all cell needs, it is not immediately responsible for the energy that is necessary for muscle contraction. Seemingly, within unfatigued muscle cells there is some readily available source of energy for this purpose, the oxygen brought by hemoglobin appearing to be in relation to the recovery period to recharge the cells, as it were, in order that they may again be ready for immediate response when stimulated.

It seems probable that simultaneously with the series of reactions whereby lactic acid is made from glycogen there is an associated series of reactions involving the hydrolysis, followed by resynthesis, of certain phosphoric acid complexes (adenosinetriphosphate and phosphocreatin). Thus, there seem to be at least two functions of phosphoric acid in connection with carbohydrate metabolism in muscle cells: (1) to react with glycogen to make hexosediphosphate (p. 465); (2) then, when it is again set free as pyruvic acid is made, to react with creatin to remake phosphocreatin or phosphagen (p. 486), a compound which is not subject to diffusion through cell membranes. At one time it was believed that it is in the course of these reactions involving the phosphoric acid complexes that the energy for muscle contraction is made and that the substance oxygen provides energy for their resynthesis. The fact of the matter is that there is a great deal not yet understood regarding carbohydrate metabolism in muscle cells.

Lactic acid. Of the lactic acid thus made, part, claimed to be about one-fifth, reacts with oxygen to make carbon dioxide and water. These reactions are presumed to take place likewise in stages and they are accompanied by the production of energy. This energy product is made — during the reactions concerned — chiefly from chemical energy within the oxygen brought to the cells by hemoglobin, and it is this energy which is required for doing the work demanded of the cells. The rest of the lactic acid, variously estimated as from three-fourths to four-fifths, is believed to be used for the rebuilding of glycogen, a mechanism which guards against the depletion of the glycogen content of the cells. Whether this resynthesis takes place in part within the muscle cells themselves or whether the lactic acid so used must all be car-

ried by the blood to the liver for the making of glycogen is an unsettled question.

A summary. Following (in part) the fate of glucose in muscle cells:

Glucose (brought to the cells by the blood)
↓ dehydrolyzed for storage
Glycogen (a portion)
↓ with phosphoric acid
Hexosephosphate
↓
Phosphoglyceric acid
↓
Pyruvic acid and Phosphoric acid
↓
Lactic acid
↓ about 1/5 reacts with oxygen from oxyhemoglobin
Carbon dioxide and Water (end products for excretion) and **an energy product.**

Lactic acid —about 4/5→ Some in liver cells → Glycogen

Lactic acid —about 4/5→ Perhaps in part in muscle cells → Glycogen (a portion)

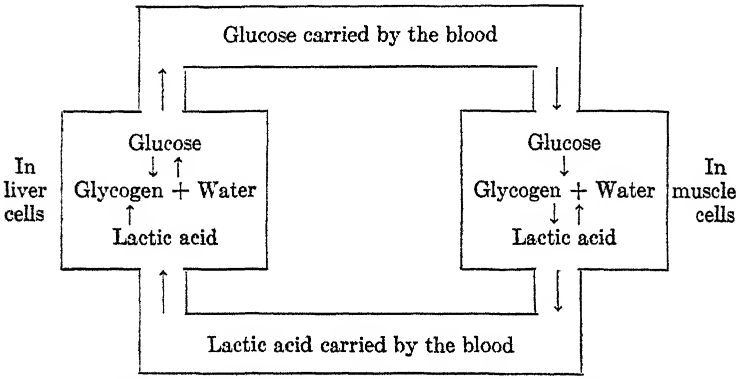
Bacterial metabolism. The so-called fermentation reactions as to glucose, which are catalyzed by enzymes produced within bacterial cells with the production of lactic acid, are believed to follow a sequence of reactions that is similar to the glycogen-to-lactic acid sequence of reactions in muscle cells.

Role of vitamin B_1 or thiamin. There is experimental evidence to support the claim that vitamin B_1, or thiamin, functions as a catalyst for reaction of oxygen with lactic acid and pyruvic acid to make carbon dioxide and water. In its absence pyruvic acid accumulates and produces symptoms that are characteristic of lack of this vitamin. And this holds not only for carbohydrate metabolism in muscle cells but in nerve cells as well. Thus, an adequate provision of vitamin B_1 in the diet results in better metabolism throughout the body.

Lactic acid and glycogen cycle. Lactic acid is present in the blood at all times, but with adequate oxygen carried to the cells, it does not accumulate in the blood but appears to be taken care of about as rapidly as it enters the circulation. During rest periods, when muscle activity is at a minimum, blood lactic acid is also at a minimum. During moderate exercise more lactic acid is made in the cells than during rest, but the accompanying stimulation of respiration and circulation carries sufficient oxygen to the cells to dispose of it promptly in the two ways previously specified. However, in the case of strenuous exercise, when the supply of oxygen provided to the cells is temporarily inadequate, lactic acid accumulates above normal quantities in the cells and blood; in this event a considerable rest period following upon such exercise may be

required before an adequate replenishing of oxygen can be established and the lactic acid reduced to its normal level. It is claimed by some that the sensation of fatigue commonly experienced in association with strenuous exercise is due to this accumulation of lactic acid, and that the gradual recovery from fatigue is contingent upon reëstablishment of an adequate oxygen supply and the resulting utilization of this excess lactic acid.

As to the fate of the lactic acid which leaves the muscle cells to enter the blood, there is experimental evidence to indicate that, although a small amount may escape into the urine, it is for the most part carried to the liver where it is used for the making of glycogen. The following diagram represents the related fates of glycogen and lactic acid in the so-called glycogen-lactic acid cycle.



Intermediate metabolism of glucose in nerve cells. Even less is known concerning the reactions by which energy is produced within nerve cells than concerning those which take place within muscle cells. However, the information which has been assembled from such research as has been done in this field points to the conclusion that the processes which go on in these two different types of cells are in many respects similar. Certainly, some of the same intermediate products have been found to be present in nerve cells as in muscle cells. One difference lies in the finding that nerve cells seemingly use glucose in the metabolic series of reactions without the appearance of glycogen as an intermediate compound. And, again, it should be stressed that, as in muscle so in nerve cells, vitamin B_1 is an essential catalyst for the reaction of oxygen with lactic and pyruvic acids (p. 467) to make carbon dioxide and water.[4]

[4] R. W. Gerard, "The Metabolism of Brain and Nerve Cells," *Annual Review of Biochemistry*, **6**, 419 (1937).

Glucose metabolism in relation to fat metabolism. It is an interesting fact that normal oxidation of glucose in the cells is essential for the normal oxidation of fat. Why this is so, and just how glucose and its metabolic intermediates function in this capacity is unknown, but it is certain that when there is faulty glucose metabolism — as is the case in diabetes, or starvation — the oxidation of fats does not proceed normally and acetoacetic acid, β-hydroxybutyric acid, and acetone appear in the blood and are excreted in the urine. The presence of these substances, known as *ketone bodies,* in the blood gives rise to a condition known as acidosis (p. 474). The functioning of glucose metabolism in preventing faulty metabolism of fats is sometimes spoken of as its *antiketogenic* action.

Glucose used to make fats. Glucose provided by the diet in excess of the immediate needs of the cells is built into fat which is deposited in the fat storage cells. This utilization of glucose to make fat obviously involves a reduction of glucose (p. 269).

Glucose used to make other important compounds. A review of the many and varied compounds which are peculiar to animal cells indicates that cells probably use glucose in the making of a variety of such essential compounds. During pregnancy and the period of lactation, milk sugar or lactose appears as a component of milk in the mammary glands. For the building of this sugar it is believed that the cells of these glands have the ability, first to make galactose from its isomer glucose, then to make the disaccharid lactose through the dehydrolysis of glucose and galactose. Other compounds within body cells, such as glycoproteins, nucleoproteins, and glycolipids, have a monosaccharid constituent; and although the monosaccharid involved does not always appear to be glucose, yet, glucose being predominantly the sugar carried to the functioning cells, it is reasonable to believe that it may be used as a source of the other monosaccharids which in turn are used for the synthesis of these compounds.

Glucose prolongs the life of cells in oxygen hunger. There is experimental evidence to indicate that the presence of an adequate glucose, or glycogen, supply within cells supports the vitality of the cells during periods of oxygen hunger. Such a condition may occur during the administration of a general anesthetic or as the result of hemorrhage with the accompanying loss of oxygen-carrying red blood cells. Therefore, the provision of a high carbohydrate diet preoperatively, as well as the administration of glucose intravenously, helps to insure an adequate supply of glucose for the

cells at such times. How glucose functions in this connection is not known.[5]

FUNCTION AND FATE OF FATTY ACIDS AND GLYCEROL

In the intestinal membrane. The end products of fat digestion which enter the intestinal membrane are fatty acids and glycerol, but the substances which emerge from this membrane into the lacteals are fats. Therefore, the making of fats in this location constitutes the first step in fat metabolism. But it is important to note that the intestinal membrane contains not only fatty acids of food origin but also fatty acids which have been made, possibly within the intestinal membrane itself, possibly in other parts of the body, and brought to this membrane. Consequently, with a different assortment of fatty acids from which to select, the fats which are synthesized in this region and which emerge into the lymph circulation, may be quite different in character from those of the original food, and more characteristic of the fats of the animal itself than of the foregoing food mass (p. 477).

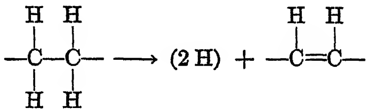
Transportation to the cells. Within a few hours after the absorption of a fatty meal the lacteals of the intestinal villi become filled with fat and the lymph leaving this region acquires a milky appearance due to the presence of this fat in a high state of emulsification. This fat-laden lymph from the intestine is emptied first into the thoracic duct, then into the superior vena cava, thereby entering the blood just before the latter passes through the heart. Why it is that the greater part of the fat is absorbed from the intestine by the lymphatics and enters the blood by this circuitous route is not known, but it has been suggested that it may be for the purpose of enabling certain fatty components to be withdrawn from the blood by the cells before the remaining fats are routed to the liver and exposed to chemical changes believed to be carried on in that organ.

It is known that in the blood stream true fats are not the only carriers of fatty acid radicals since they are conveyed also by phospholipids (p. 373) and by cholesteryl esters of fatty acids. These fats, phospholipids, and cholesteryl-fatty acid esters are distributed by the blood to *all* cells throughout the body: the fat storage cells, and the active cells including those of the liver.

Fats are desaturated in the liver. Liver fat is always highly unsaturated. It follows, therefore, that the fatty acid radicals of fats and phospholipids that are carried to the liver must undergo

[5] A. P. Mathews, *Principles of Biochemistry*, Wm. Wood & Co., 1936, p. 62.

a dehydrogenation in order to accomplish this greater desaturation. Theoretically, this would mean that within fat molecules thus affected, single bonds between selected pairs of carbon atoms must give way to double bonds at some points within the fatty acid chains:



Fats and cell components. Fats or fat derivatives, chief among which are phospholipids, together with proteins, comprise the major components of the protoplasm of the cells. Fat derivatives may also be components of the intracellular material; certainly they contribute to the structure of cell walls, and they are believed to be partly responsible for the permeability of these containing membranes.

Fats as partner substances with oxygen to produce energy. It is a well-established fact that, within the cells of muscle and other tissues, fats, as well as glucose, provide partner substances for reactions with oxygen during which the energies essential for cell activities are made. And it is known that one gram of fat is responsible for engaging 2.9 grams of oxygen to make carbon dioxide and water and that during the reactions concerned 9.45 Calories of energy product is made (p. 79):

1 gram Fat	+	2.9 grams Oxygen	⟶	Carbon dioxide	+	Water		
↓		↓		↓		↓		
Chemical energy	+	Chemical energy	⟶	Chemical energy	+	Chemical energy	+	***9.45 Calories of kinetic energy,*** heat, or other energy required by the cells.

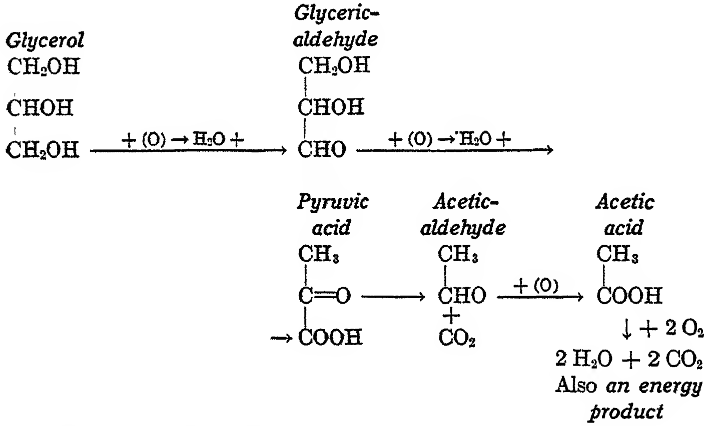
A comparison of the quantities of oxygen engaged by one gram of glucose and one gram of fat to make carbon dioxide and water reveals the interesting fact that they are almost in direct proportion to the quantities of energy products made. It is this quantitative relationship of oxygen used and energy products made that leads to the reasonable conclusion that the major source of energy product is probably from part of the chemical energy of the previously existing oxygen, very little being made from the chemical energy of the glucose or fat.

Intermediate metabolic steps. The foregoing equation mentions only the outstanding substances existing before the reaction begins: namely, fats and oxygen, and the substance end products,

carbon dioxide and water. Just what intermediate substances are made and through what reactions is still obscure. However, certain suppositions, developed from various experimental studies, have been arrived at which it will be interesting and enlightening to consider.

The first reaction in fat catabolism in the cells is believed to be one of hydrolysis with the usual glycerol and fatty acids as products. From then on these substances follow separate metabolic paths. Let us follow first the supposed fate of glycerol.

Oxidation of glycerol. Some of the glycerol obtained in the cells from fat hydrolysis may be used for making other substances, notably glucose (p. 475). But our interest at present is in the reaction sequence which at some point provides a reacting partner for oxygen, and it is this sequence which is represented in the following:

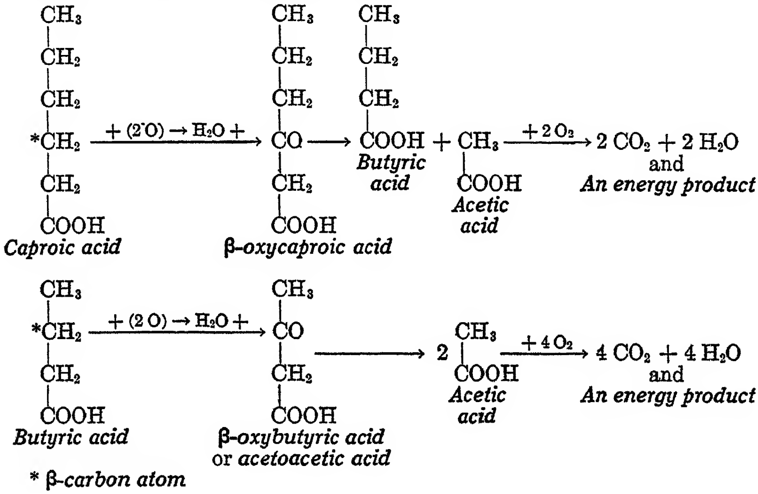


Oxidation of fatty acids. In regard to the fate of fatty acids in the cells, the theory most generally accepted was developed by Knoop about 1904 and is supported by considerable experimental evidence. This theory, known as the beta-oxidation theory, supposes that an oxidative attack takes place at the beta carbon atom of the fatty acid molecule, that is, the second carbon atom beyond the carboxyl group, to make a ketone. This is believed to be followed by a similar oxidation at the ketone group, but accompanied this time by a break in the carbon chain whereby a *shorter chain fatty acid and acetic acid are made.* Then the whole series of reactions is repeated with each shorter chain fatty acid thus arrived at. Accordingly, a sixteen carbon atom fatty acid molecule gives way to a fourteen carbon atom fatty acid molecule, which in turn gives

way to a twelve carbon fatty acid molecule, etc., with an acetic acid molecule being made at each cleavage stage. Such a possible sequence of events in the progressive oxidation of a fatty acid molecule beginning at the six carbon atom fatty acid stage is represented below.

Several other theories, based likewise on experimental evidence, have been proposed to account for the oxidation of fatty acids, and it is possible that more than one type of attack may take place in the process.

Oxidation of a typical fatty acid molecule

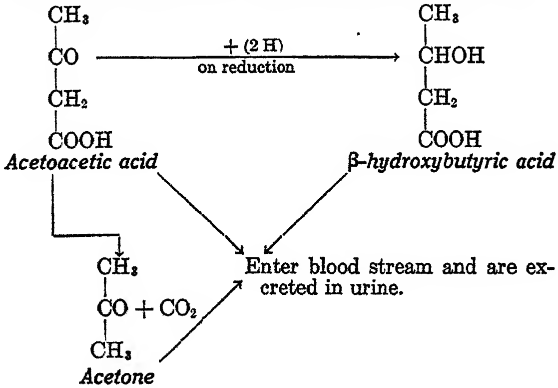


Ketosis results from faulty fat metabolism. As stated previously in connection with glucose metabolism (p. 469), it is a well-established fact that the oxidation of fats does not proceed normally through all stages to the end products carbon dioxide and water unless associated with the normal oxidation of glucose. If for any reason glucose is not being oxidized within the cells, then faulty fat metabolism sets in and this is accompanied by an accumulation in the blood of beta-hydroxybutyric acid, acetoacetic acid (diacetic acid), and acetone (p. 474), and by their excretion in the urine. These three substances are known as "ketone bodies," although it should be noted that beta-hydroxybutyric acid is not a ketone, and the condition produced in the body is called *ketosis*. This condition is most commonly associated with diabetes, in which disease the cells are unable to utilize all of the glucose brought to them by the blood; but it is also associated with starva-

tion, in which condition the glucose-glycogen supply of the cells may become exhausted. Ketosis has also been reported to occur temporarily in persons doing strenuous muscular work on a low carbohydrate intake.[6]

The appearance of these ketone bodies, together with glucose, in the urine provides a reason for believing that fatty acid oxidation can proceed normally until acetoacetic acid stage is reached; but from this point on, fatty acid oxidation can continue only in the presence of normal glucose metabolism. At this stage part of the acetoacetic acid (diacetic acid) may be reduced to make β-hydroxybutyric acid, while part decomposes to make acetone and carbon dioxide. This proposed sequence of reactions is represented as follows:

Changes that may occur in case of faulty fat metabolism



Although traces of these three compounds, especially acetone, are not unusual in normal urine, their excretion in large quantities is of pathological significance. If the condition is severe, acetone may be detected on the breath by its sweetish odor. The presence of acetoacetic acid and beta-hydroxybutyric acid in the blood tends to increase the concentration of hydrogen ions therein slightly above normal, thus giving rise to the condition known clinically as acidosis (p. 504).

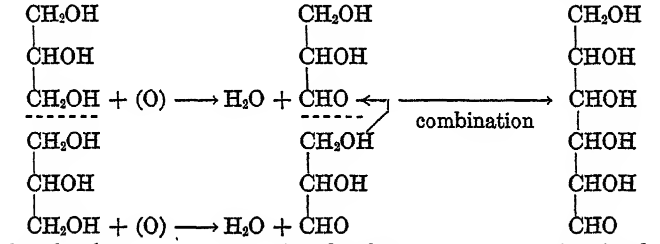
Before the discovery and clinical use of insulin, acidosis, frequently associated with coma, was an all too common complication in diabetes. The reason for this was that the diabetic, being unable to oxidize glucose, was fed on a high fat diet with very little carbohydrate, and under these conditions, ketosis was not unlikely to develop. Indeed it was looked upon as almost inevitable that a severe diabetic would sooner or later develop this almost unavoidable and often fatal complication. Today the situation is greatly changed. The

[6] Meyer Bodansky, *Introduction to Physiological Chemistry*, John Wiley & Sons, 1938, p. 369.

use of insulin makes possible the normal oxidation of glucose, as a result sufficient carbohydrates can now be provided in the diet to establish a satisfactory antiketogenic carbohydrate-fat balance. Diabetic acidosis is now looked upon as a preventable complication, and even if acidosis does occur, it can be treated successfully by providing the necessary glucose along with insulin to assure its antiketogenic functioning.

Within recent years this knowledge of the glucose-fat metabolic relationship has been made use of for other therapeutic purposes. Thus in some pathological conditions a ketone-producing, or *ketogenic diet,* is prescribed: namely, a diet in which the proportion of fat to carbohydrate is deliberately adjusted in such a way that ketosis is produced. A study of these ketogenic diets shows that they are essentially high fat diets inadequately balanced with carbohydrate. Such diets are used to some extent in the treatment of epilepsy.

Fats used in the cells to make glucose. Fats, or the intermediate products of fat metabolism, can be used by the cells to a certain extent to make glucose. It is generally agreed that the glycerol obtained from the hydrolysis of fats can be so used, perhaps after the manner suggested by the following equations:



2 molecules of glycerol — *2 molecules of glyceric aldehyde* — *1 molecule of glucose*

It is not known whether fatty acids, likewise obtained from the hydrolysis of fats, can be used for the synthesis of glucose.

Fat of active tissues. In active cells the fat-like substances, phospholipids (p. 373), predominate over true fats; and the fatty acid radicals that both carry as constituents are *highly unsaturated,* having been desaturated probably in the liver. This is doubtless a most significant fact since unsaturated fats and phospholipids are much more active chemically than they would be otherwise, and active cells seemingly should be able to use them to better advantage than saturated, hence less active, lipids.

The fats of storage cells. There is some evidence that the major portion of fats which enter the blood stream may be selected first by fat storage cells to be drawn upon as needed by the more active cells. Although this stored fat may be widely distributed throughout the body, it is especially likely to be deposited in the

connective tissue layer directly under the skin, in the omentum which covers and protects the abdominal organs, and as packing around the kidneys.

Sources. The animal draws its storage fat from two main sources, the *fats of the food* supply and *from glucose* which is made both from carbohydrate foods and from other substances within the body when present in excess of metabolic needs. That there is a relationship between food intake and fat storage is a matter of common experience, since it is a well-known fact that a diet in which carbohydrates and fats appear in abundance is followed by fat deposits in the fat storage cells. A third but limited source of fats appears to be *from certain amino acids* of protein origin, although this source may possibly be by way of glucose first made from these acids.

Fats from glucose. One location where fats are made from glycerol and fatty acids has already been considered (p. 470): namely, in the intestinal membrane. But where and how fats are made from glucose is not known. However, whatever the process may involve, it is reasonable to suppose that glycerol and fatty acids may be first made and that the fats follow from the dehydrolysis of these substances. It would seem a rather simple undertaking for nature to make *glycerol* from any one or all three of the glucose metabolic intermediates, glyceric aldehyde, pyruvic acid, or lactic acid. Thus:

$$\begin{array}{lcl}
CH_2OH & & CH_2OH \\
| & & | \\
CHOH & & CHOH \\
| & & | \\
CHO + & (2\,H) \longrightarrow & CH_2OH \\
\textit{Glyceric} & & \textit{Glycerol} \\
\textit{aldehyde} & &
\end{array}$$

But it is more difficult to understand how the *fatty acid* can be obtained from glucose origin. Various theories are advanced to account for this synthesis, one of which assumes that the fatty acid results from a condensation of a series of *acetaldehyde* molecules, which are likewise glucose metabolic intermediates. The following represents how butyric acid, the simplest of the fatty acids, may be made after this manner:

$$\begin{array}{lclcl}
CH_3 & & CH_3 & & CH_3 \\
| & & | & & | \\
CHO & & CHOH & & CH_2 \\
 & \longrightarrow & | & \longrightarrow & | \\
CH_3 & & CH_2 & & CH_2 \\
| & & | & & | \\
CHO & & CHO & & COOH \\
\textit{Acetaldehyde} & & & & \textit{Butyric acid}
\end{array}$$

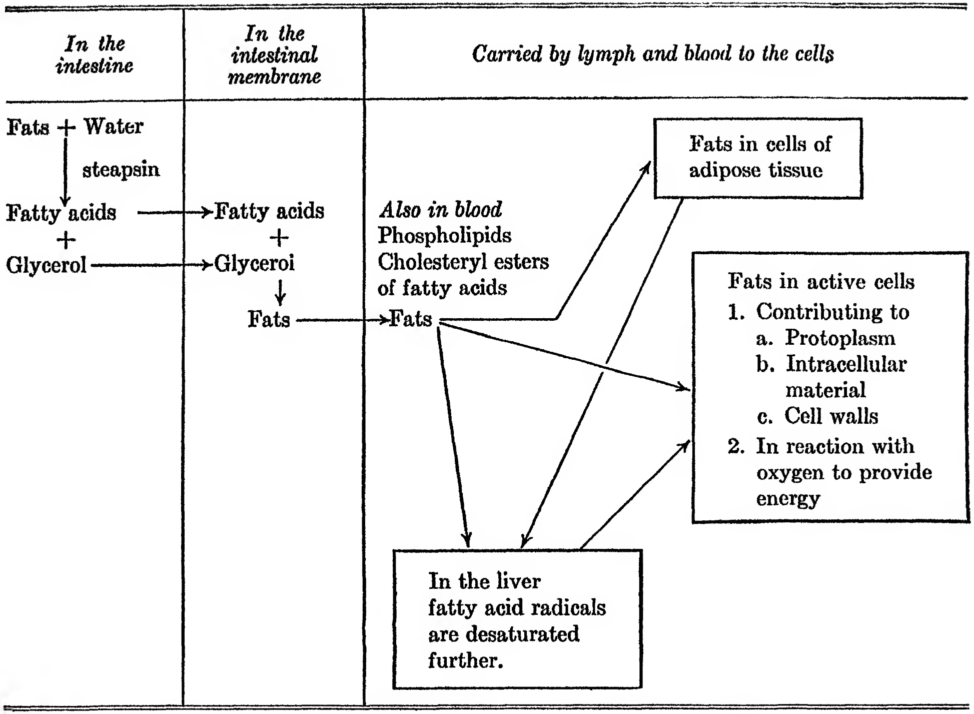
Repeated condensations after like manner would result in fatty acids of still longer chains. This theory, if correct, would mean that all fatty acid molecules made thus would, of necessity, be composed of carbon atoms in multiples of two; and this is a condition which fits in admirably with factual findings in that practically all fats of natural occurrence in animal cells do indeed contain even numbers of atomic weights of carbon. (See formulas for fatty acids, p. 333.)

Character of storage fat. The mixture of fats and fat-like substances that is characteristic of fat storage differs from that in active cells in that true fats predominate over phospholipids and both are largely *saturated*. Storage fat is usually different in character from the fats of the food supply; indeed the animals of a given species fed on their customary mixed diet, build a storage fat that is peculiar to them. For example, the lard of pigs differs in character from the mutton tallow of sheep, and both differ from the beef tallow of cows; fish fat differs from that of land animals; and human fat is peculiar to humans. Why such is the case is not known, but it has been suggested that the similarity in diet of members of the same species may be a factor. This view finds support in the results of feeding experiments with various animals which have shown that the character of stored fat can be modified to some extent by a selection of their food; for instance it has been found that animals fed on cottonseed oil develop a soft fat which resembles that of their food, whereas animals fed on corn deposit a harder and more saturated fat, made in this case from carbohydrate.

Functions of storage fat. Storage fat, if not in excessive amount, is an important asset to the animal. (1) It is one of the provisions whereby the body is able to maintain a fairly constant temperature. Fats are poor conductors of heat, hence the fat layer which underlies the skin provides insulation, thereby preventing too rapid radiation of heat from the body surface. (2) An important function of the fatty layers which normally surround certain vital organs, such as the kidneys, is that of providing support for these organs and protection from injury.

(3) But the primary function of storage fat would seem to be that of providing a reserve food supply upon which the actively functioning cells can draw as required. Certain it is, that in starvation when the external food supply is inadequate to meet the metabolic needs of the animal, although stored fat never completely disappears, its accumulation is depleted, the fat being conveyed

Diagrammatic summary of the fate of fatty acids and glycerol in the body



first to the liver for a greater degree of desaturation, then to the active cells for all the uses for which fats are essential.

In summary. A partial summary of the function and fate of glycerol and fatty acids is given in the tabulation on page 478.

FUNCTION AND FATE OF AMINO ACIDS

The various amino acids, end products of the digestion of proteins, are absorbed from the intestine into the portal circulation and carried by way of the liver to the general circulation for distribution to cells of the various tissues. Normally there is never a high concentration of amino acids in the blood, nor do they accumulate to any great extent in the cells. Moreover, within a few hours after a meal high in protein content, urea, the outstanding product of protein metabolism, appears in the urine in a quantity proportionate to the quantity of protein intake. These facts seem to indicate that the cells remove amino acids from the blood stream almost as rapidly as they enter this medium from the liver, and that the amino acids within the cells are promptly subjected to the metabolic reactions involved in their utilization and disposal.

Sources of amino acids in the cells. The chief source of amino acids in the cells is from those brought to it by the blood. However, in addition to these, amino acids are made in the cells themselves as products of the hydrolysis of proteins of protoplasm in the course of cell metabolism, a process which is continually in operation:

$$\text{Cell proteins} + \text{Water} \rightarrow \text{Amino acids}$$

And certain of the less complex amino acids, such as alanine, are believed to be made in the cells by reaction between ammonia and selected intermediate products of the metabolism of glycogen, possibly pyruvic acid, or lactic acid. The following represents such a presumable reaction on the part of a molecule of pyruvic acid:

$$\text{Pyruvic acid} + \text{Ammonia} \longrightarrow \text{Alanine} + \text{Oxygen compound}$$

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ COOH \end{array} + NH_3 \longrightarrow \begin{array}{l} \ \ \ CH_3 \\ \ \ \ | \\ HC{-}NH_2 \\ \ \ \ | \\ \ \ \ COOH \end{array} + (O)$$

Certain amino acids, such as alanine, may be made from pyruvic acid as a glucose metabolic intermediate.

Amino acids are essential to the building of tissue. The primary function of amino acids in the cells is for the building of the specific

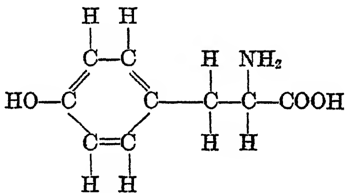
varieties of proteins that are, in turn, essential to the synthesis of the cells' protoplasm. Just how this protein building is accomplished is not known, but it is reasonable to suppose that it may be through a dehydrolysis of amino acids (p. 336) favored by specific catalysts provided in the cells. The proteins which are made vary, not only in different tissues of the same animal, but also in corresponding tissues of different animal species. This necessitates an ability on the part of the various cells to select from the many amino acids brought to them, the particular assortment and relative quantities of amino acids that are essential to the building of their own specific proteins; and unless these necessary amino acids are provided, and in sufficient amounts, the life and growth of the cells cannot proceed normally (p. 418). Consequently, since most of the amino acids are provided by protein components of the food mass, this requirement has a nutritional significance. Not only must the daily diet provide an adequate amount of proteins, but these proteins must be of such variety as to insure the inclusion of all the essential amino acids.

The repair of proteins takes place at all times for the renewal of such proteins as become involved in cell catabolism of already existing tissues; but over and above this continuous need there are times when protein synthesis must also take place for the making of new cells for new tissue. It follows, therefore, that the demand for amino acids must vary, depending upon the extent to which proteins must be repaired and new ones made.[7] Thus, in the healthy adult of moderate muscular activity only protein replacement takes place; this involves the daily repair and making of only a very small proportion of body tissues,[7] consequently, a correspondingly limited supply of amino acids is required. But during the growth period there is a much greater demand for amino acids to meet the needs for protein synthesis, not only for the maintenance of already existing tissues, but also for the making of new tissues. And there are conditions under which even adults require a larger than normal supply of amino acids for protein synthesis. Some of these conditions are as follows: (1) when the healthy adult becomes engaged in excessive muscular exercise for a considerable length of time the need arises for the making of more than the usual amount of muscular tissue; (2) when the individual is recovering from an illness which is accompanied by a wasting away of tissues, or a loss of cells through hemorrhage, recovery

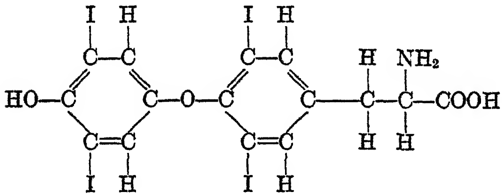
[7] Daily requirement for normal adult is 5 grams of protein per kilogram of body weight. Sherman, *Chemistry of Food and Nutrition*, The Macmillan Company, 1941, p. 202.

calls for the making of new cells; (3) when the adult has met with injury involving tissue destruction, such as a serious burn, recovery likewise necessitates the making of new cells.

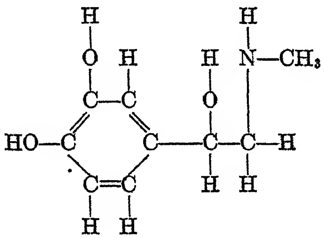
Amino acids for making other essential substances. Certain amino acids are required for the building of essential substances, such as enzymes and hormones, which are made in specific locations within the body. For example, tyrosine, cystine, glutamic acid, arginine, leucine, and lysine must be selected by the cells concerned, for the making of insulin in the pancreas; tyrosine must be selected for the making of thyroxine in the thyroid gland and of epinephrine in the adrenal glands:



Tyrosine



Thyroxine



Epinephrine (or *Adrenalin*)

Tyrosine is also claimed to be necessary to the making of melanin, the dark pigment which gives color to hair, eyes, and skin, so especially evident in the dark races.

Amino acids with oxygen in the production of energy. Although not their primary function, amino acids in excess of cell needs are also used as partner substances with oxygen to provide energy. The matter products of such reactions are carbon dioxide, water, and nitrogenous products of which the most important is urea. It has been calculated that for every gram of protein thus used in

providing amino acids for reaction with oxygen, an energy product of approximately 4.35 Calories is made:

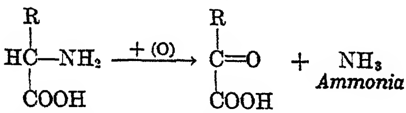
1 gram (av.) Protein	+	1.23 grams (av.) Oxygen	→	Carbon dioxide	+	Water	+	Urea		
↓		↓		↓		↓		↓		
Chemical energy	+	Chemical energy	→	Chemical energy	+	Chemical energy	+	Chemical energy	+	***4.35 Calories kinetic energy*** or other energies needed by the cells.

In case of an inadequate diet, whereas storage fat constitutes the first reserve to be drawn upon for food for the cells, evidence is provided through the attendant emaciation that, lacking such fat reserve, the proteins of the tissues can be utilized toward such end.

Intermediate metabolism of proteins. It is not to be assumed, however, that oxygen reacts directly with the proteins. Instead, it is believed that various intermediate reactions take place, perhaps somewhat as follows:

1. The cell proteins undergo hydrolysis to make amino acids with proteolytic enzymes in the cells acting as catalysts.

2. The amino acids that result from these reactions in the cells, together with other amino acids in the blood which are in excess of those needed by the cells for building protein, are distributed to the liver, kidneys, and intestinal mucosa, where they undergo deaminization and oxidation to make *ammonia and keto-organic acids,* perhaps after the manner suggested in the following equation:



An amino acid *A keto acid*

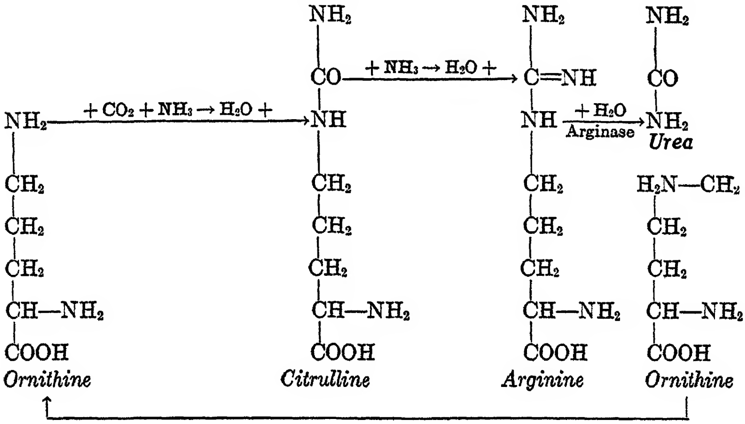
From then on two sets of reactions set in, one in respect to ammonia, the other in respect to the organic acid.

Fate of the ammonia. Most of the ammonia disappears rapidly in the making of urea ($NH_2—CO—NH_2$), probably in the liver. The intermediate reactions concerned are not known, but a theory of recent date, and one which has been received with considerable favor, suggests that: (1) ammonia reacts with carbon dioxide and ornithine to make citrulline and water; (2) the citrulline thus made reacts with more ammonia to make arginine and water; and

(3) finally arginine reacts with water to make urea and remake ornithine, which is free to begin the cycle of reactions over again with more ammonia. These reactions are believed to be catalyzed, with arginase functioning as catalyst for the making of urea from arginine. This reaction sequence on the part of the molecules concerned is represented below.

Urea is very soluble in water, therefore the body encounters no difficulty in carrying it by way of the blood to the kidneys, chiefly, and to the skin where it is eliminated.

Fate of Ammonia



Evidence that urea is made in the liver. On the removal of the liver from experimental animals it has been found that the concentration of urea in the blood is decreased and that amino acids accumulate and are excreted in the urine. In other experiments performed on dogs it has been observed that, after an operation known as Eck's fistula has been performed, as the result of which the blood passes directly from the intestine to the general circulation instead of through the liver, urea fails to be made and ammonium compounds accumulate in the blood.

Ammonia and ammonium salts. Although ammonia is made in the deaminization of amino acids in various parts of the body, ammonium salts are not normally present in the blood to any appreciable extent. Therefore, the fact that they are present in relatively high concentration in urine has led to the belief that *ammonia must be made in the kidney cells themselves,* possibly from deaminization of amino acids and purines, possibly from urea. Presumably, then, it is this ammonia that leads to the ammonium salts that are excreted in the urine.

Fate of the keto organic acid. The keto organic acids that result from this deaminization of amino acids in the liver, kidneys, and intestinal mucosa are possibly distributed to the active cells where they become involved in a series of oxidative reactions. These reactions may differ in some respects for the keto acids that are derived from different amino acids; but they are similar in that each acid is believed to react with an oxidizing agent at the keto-carboxyl linkage to make carbon dioxide and acetic acid, while the latter, in turn, is oxidized to make carbon dioxide and water. Such a series of reactions on the part of a molecule of the amino acid alanine is represented as follows:

In liver, or kidney, or intestinal mucosa | *In active cells*

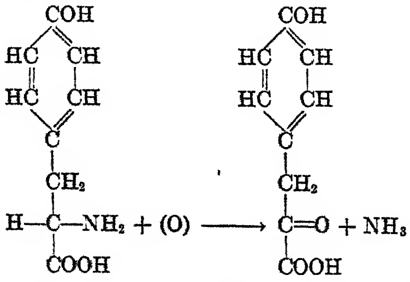
$$\underbrace{\begin{matrix} CH_3 \\ | \\ CH{-}NH_2 \\ | \\ COOH \end{matrix} \xrightarrow{+(O) \rightarrow NH_3 +} \begin{matrix} CH_3 \\ | \\ CO \\ | \\ COOH \end{matrix}} \quad \underbrace{\xrightarrow{+(O)} \begin{matrix} CH_3 \\ | \\ COOH \\ + \\ CO_2 \end{matrix} \xrightarrow{+2O_2} \begin{matrix} 2\,CO_2 + 2\,H_2O \\ \text{also} \\ \textit{An energy product} \end{matrix}}$$

The matter products of these reactions, carbon dioxide and water, are eliminated in the usual manner. And as usual the chief energy product is obtained at the reaction stages where oxygen, released from oxyhemoglobin, becomes involved.

When the amino acid contains a cyclic structure. Oxidation of keto-acids that are derived from such amino acids as tyrosine and phenylalanine, whose molecules contain cyclic groups, must involve some process by which the ring structure is broken. This is difficult to bring about in test tubes and beakers but apparently nature accomplishes this feat without difficulty in animal cells.

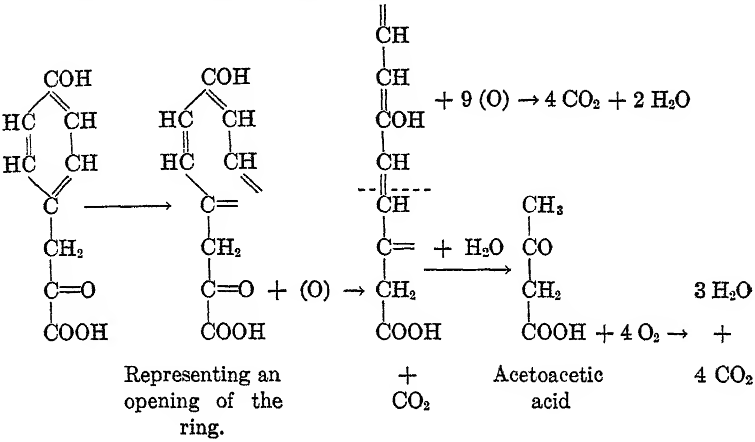
The following equations represent one concept as to the possible sequence of reactions involved in the metabolism of a molecule of tyrosine.[8]

1. Preliminary deaminization of the amino acid



[8] H. D. Dakin, ***Oxidations and Reductions in the Animal Body***, Longmans, Green and Co., 1922, pp. 84–88.

2. Oxidation of the resulting organic acid



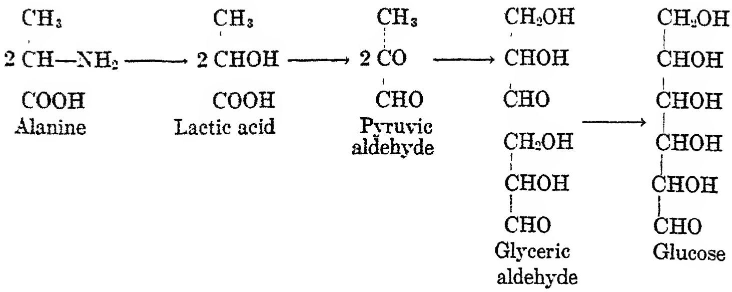
Evidence indicating that acetoacetic acid may be one of the intermediate products of the metabolism of phenylalanine, also of tyrosine, is provided in the finding that when diabetic animals are fed on phenylalanine or on tyrosine they excrete increased amounts of acetoacetic acid in the urine.[9]

Synthesis of glucose from amino acids. There is considerable experimental evidence to indicate that certain of the amino acids can be used in animal cells for making glucose. The most outstanding contribution in this connection is that of Graham Lusk and his students, who worked with dogs rendered diabetic by the use of phlorizin.[10] These dogs having been starved until their supply of glycogen was depleted were fed exclusively a mixture of amino acids obtained by the hydrolysis of the proteins of meat. But it was found that they continued to secrete glucose which it seemed obvious must have been made from the amino acids. Later experiments, similar in nature, gave evidence that only certain amino acids can be utilized in the cells in this way, among them glycine, alanine, cystine, arginine, and aspartic acid.

There is a great deal of uncertainty as to the intermediate steps that are involved in this making of glucose from amino acids, but some evidence has been obtained in support of the suggestion that the possible sequence of changes, which begin with alanine, are as represented in the following:

[9] J. S. R. MacLeod, *Physiology in Modern Medicine*, The C. V. Mosby Company, pp. 631, 666.

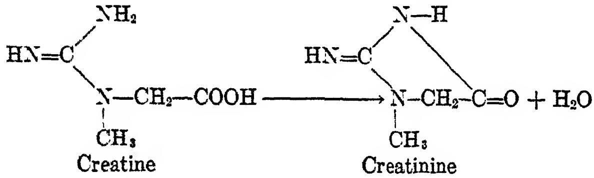
[10] Graham Lusk, *The Elements of the Science of Nutrition*, W. B. Saunders Company, 1928, pp. 207, 231.



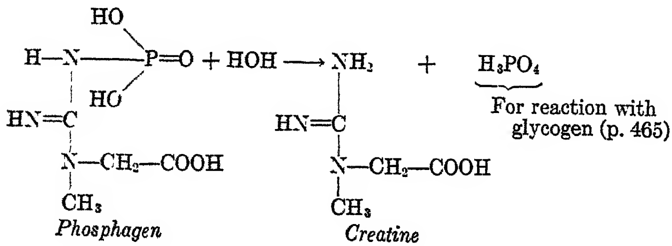
Summary as to fate of amino acids. See the opposite page.

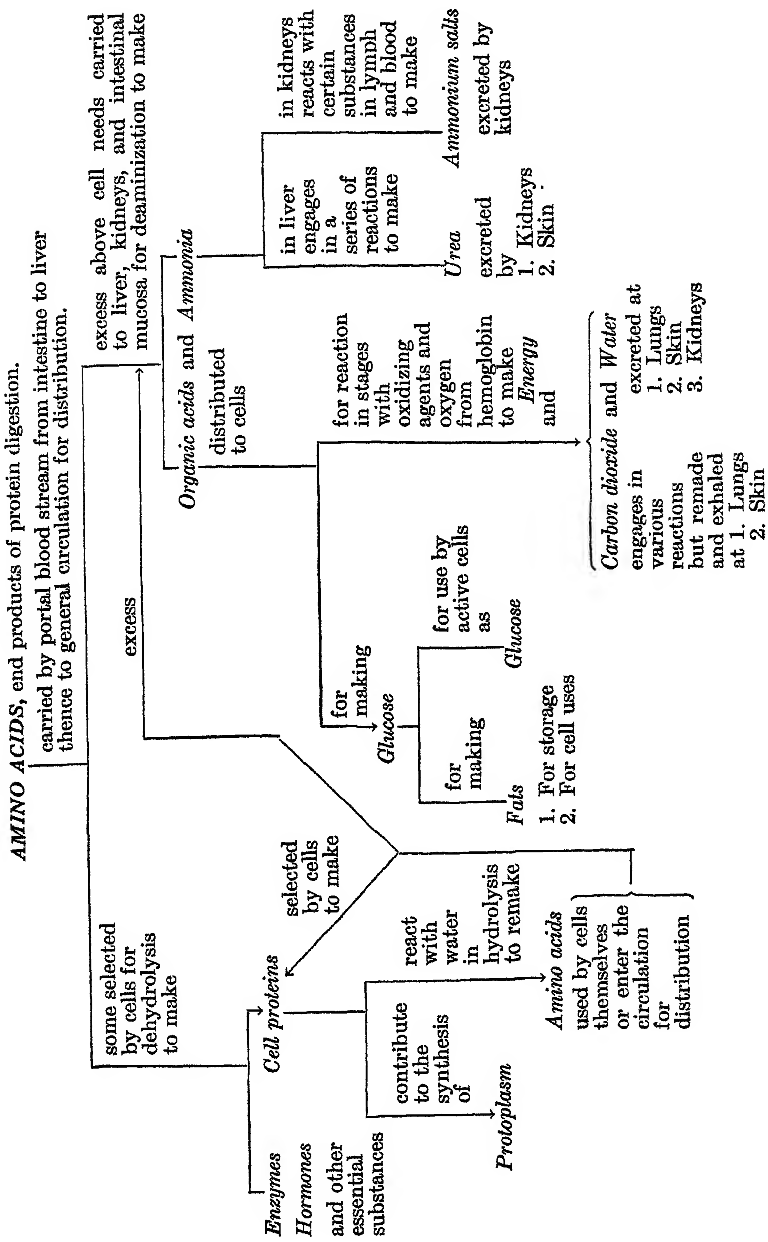
CREATINE AND CREATININE

Like proteins these are nitrogen-containing compounds. They are related to each other in that creatinine is the anhydride of creatine, from which it is very easily made through dehydrolysis.



Creatine. Creatine is widely distributed in all animal tissues but, in association with phosphocreatin, it is especially abundant in muscle cells where, together, they constitute about 0.4 per cent of cell contents. Both are believed to be physiologically important in these tissues in relation to muscle contraction (p. 466). When muscle is at rest nondiffusible phosphocreatin, known as *phosphagen,* is in predominance. During muscle contraction phosphagen is hydrolyzed to make creatine and phosphoric acid with an accompanying energy product:




AMINO ACIDS, end products of protein digestion.
carried by portal blood stream from intestine to liver thence to general circulation for distribution.
some selected by cells for dehydrolysis to make
Cell proteins
Enzymes
Hormones
and other essential substances
selected by cells to make
contribute to the synthesis of
Protoplasm
react with water in hydrolysis to remake
Amino acids
used by cells themselves or enter the circulation for distribution
excess
excess above cell needs carried to liver, kidneys, and intestinal mucosa for deaminization to make
Organic acids and Ammonia
distributed to cells
for making
Glucose
for use by active cells as
Glucose
for making
Fats
1. For storage
2. For cell uses
for reaction in stages with oxidizing agents and oxygen from hemoglobin to make
Energy
and
Carbon dioxide and Water
engages in various reactions but remade and exhaled at 1. Lungs 2. Skin
excreted at 1. Lungs 2. Skin 3. Kidneys
in liver engages in a series of reactions to make
Urea
excreted by 1. Kidneys 2. Skin
in kidneys reacts with certain substances in lymph and blood to make
Ammonium salts
excreted by kidneys

Creatine occurs not only in muscle cells but in other cells as well and may have other functions within the body. The problem of its functioning has been carefully studied by a number of observers, often with conflicting results; therefore much concerning this subject is still to be ascertained. It is known to be present in blood and lymph. It is a normal component of the urine of children and of young adults, but it does not appear in the urine of adult men who have reached muscular maturity; it persists intermittently in the urine of women.

The origin of creatine in the body is obscure; but there is some evidence to support the claim that it is made from certain amino acids: possibly from glycine and arginine.

Creatinine. This compound appears to be the chief end product of creatine metabolism. As such it is present in the blood in relatively constant quantities which range normally from about 1 to 1.5 milligrams per 100 cc. of blood. An increase in this quantity from 2 milligrams should lead to serious investigation as to cause. It is excreted in the urine of which it is a normal component. The quantity excreted is fairly constant for the individual and is in proportion to the muscular development of the subject, being highest for men who are well developed muscularly (24 to 25 milligrams per kilogram of body weight daily), but lower for men who are muscularly less well developed. For women the creatinine output is obviously less than that of men (averaging about 18 milligrams per kilogram of body weight daily); for children the average creatinine output is still lower.

Creatinuria. The excretion of creatine by men and its excretion in excess of normal by women and children, is of pathological significance and is referred to as creatinuria. This condition occurs in diabetes, as might be expected, since creatine plays a part in the normal cycle of events in respect to glucose metabolism; it occurs also in starvation, in hyperthyroidism when basal metabolism is increased, and in diseases, such as poliomyelitis, which are accompanied by muscular dystrophy.

Questions

1. What various paths do glucose, fatty acids and glycerol, and amino acids respectively follow upon their absorption from the intestine until they reach the active cells of muscle and other tissues?

2. What is believed to be the function of the liver in relation to the metabolism of (a) glucose, (b) fats, (c) amino acids? Illustrate by means of specific reactions that are believed to take place in the liver cells.

3. What is believed to be the major function of the glucose carried to the muscle and nerve cells? What partner substance is essential for this functioning and why? What are the end products of the reactions concerned? Name several important metabolic intermediates.

4. Account for the appearance of lactic acid in the blood. What is the effect of exercise? Give reason. What is supposed to be the fate of this lactic acid?

5. What is the normal concentration of glucose in the blood? What disease is characterized by an increase in "blood sugar"? To what is this abnormal increase attributed? What effect does the administration of insulin have on this condition? What effect is produced by an overdose of insulin? When adrenalin (epinephrine) is administered in the treatment of "insulin shock" what is the effect on glucose metabolism?

6. Outline three possible reaction sequences which might befall a fat molecule from the time it leaves the intestinal membrane until the end products of its metabolism are finally eliminated.

7. Under what conditions may a normal animal be expected to store fat? What are the functions of the fat so stored?

8. Represent the possible sequence of reactions by which: (a) fats may be made from glucose, (b) glucose may be made from fat.

9. Ketosis is indicative of a mutual disturbance of the normal metabolism of glucose and fat. Answer the following questions in the light of this fact:

(a) What is ketosis and with what clinical conditions is it most frequently associated?
(b) What laboratory findings are indicative of ketosis?
(c) Trace by means of formula equations the possible sequence of reactions by which the three so-called "ketone bodies" may be made from butyric acid.
(d) Why does ketosis tend to produce acidosis?
(e) How does the administration of glucose, together with insulin, function to check ketosis?

10. What are the primary functions of the amino acids provided by the proteins of the diet? During what period of life is the need for these foods greatest and why? How does the body utilize the amino acids not required for these specific needs?

11. Assemble word equations for the reactions by which energies are produced, for the work of the cells, through the reactions of oxygen with glucose, fats, and proteins. What quantity of oxygen becomes involved in reaction with one gram of each of these substances? What quantity of energy product is made during each reaction? What is the source of the energy thus produced? What variety of energy must be made for the functioning of muscle cells? What becomes of this energy? What evidence is provided by the quantitative data given to support the statement that the oxygen entering into the reaction is largely responsible for the energy product? What are the matter products and what becomes of them?

12. In making metabolic studies the oxygen intake and the carbon dioxide output are measured. Explain why such data should make it possible to calculate the energy output of the individual.

CHAPTER XXXI

Important Physiological Functionings of Salts and Their Ions

" One would naturally expect that living matter might contain some very rare, peculiar and costly metal, or substance, like radium, to which its properties might be attributed. But quite the contrary seems to be the case. Besides water, the inorganic constituents of protoplasm are salts, and they are among the commonest salts on the surface of the earth."

Albert P. Mathews, *Physiological Chemistry,* 5th Ed., p. 14.
By permission of Williams and Wilkins Company, publishers.

Salts which contribute to the make-up of the human body are as necessary to the life and normal functioning of the animal as are the substances of carbohydrate, fat, and protein origin. And although some of these salts are needed only in minute quantities, should these minute amounts be decreased below normal requirements the effects on health and life of the animal may be quite as disastrous as a deficiency in other substances that are required in greater abundance. This fact is strikingly illustrated by the disturbance of the function of the thyroid gland and the development of goiter when there is a deficiency of iodine-containing compounds, even though as little as one milligram of iodide salts per day in the diet of the average person is adequate for preventing these difficulties. Again, of copper salts the body seems to need a mere trace; indeed, it cannot tolerate these salts in larger amounts, yet this trace seems to have a very important effect on the formation of hemoglobin.

Sources of salts. Before entering further into the functioning of the various salts and their ions let us consider where the body obtains these substances for its use. On first thought one might be led to the hasty conclusion that, of course, they are obtained as salts carried into the body with the food supply and such is the source of some of them, as, for example, sodium chloride. But certain other salts or salt radicals, sulfate, carbonate, and phosphate radicals among them, are made in the cells as products of metabolism.

The following table includes some of the most important of the salt radicals — together with some indication of their sources —

which normally occur in the blood, lymph, and cells and which are considered to be essential to the normal functioning of a healthy body.

Salt radicals	*Chief sources*
Sodium	Chiefly obtained from the sodium chloride added to the food mass.
Potassium	Furnished largely by potassium salts in meat and to a less extent by such salts in fruits and vegetables.
Calcium	Provided chiefly by the calcium salts in milk; also in vegetables, although seemingly in a form less readily available for use.
Magnesium	Abundant in the cells of both plants and animals, hence furnished by both meats and vegetables.
Iron [1]	Probably both ferrous and ferric compounds can be utilized. Particularly provided by meats, egg yolk, and green vegetables.
Copper	Required only in very small amounts which are apparently adequately provided in any ordinary mixed diet. Liver and oysters are especially rich sources of this element.
Chloride	Chiefly obtained from the sodium chloride taken with the food.
Iodide	Furnished chiefly by sea salts, either through eating salt water foods or through the use of vegetables and water coming from areas where these salts are found in the soil.
Sulfate	Made in the cells from the amino acids cystine and methionine in the course of the metabolism of proteins.
Phosphates a. Phosphate b. Monohydrogen phosphate c. Dihydrogen phosphate	Obtained from the metabolism of nucleoproteins and phospholipids, also to some extent absorbed from the intestinal tract as a product of the digestion of nucleoproteins and phospholipids of the food mass.
Carbonate and Bicarbonate	Made in the process of cell metabolism from carbon dioxide and water, end products of the metabolism of glucose, fats, and proteins.
Lactate	Made in all muscle cells (and probably in other active cells) in the course of the metabolism of glycogen.

[1] Experimental evidence seems to indicate that the iron constituent of hemoglobin is not available for the use of the cells in building new hemoglobin. Sherman, Elvehjen, and Hart, *J. Biol. Chem.*, **107**, 383–394 (1934).

Salts function in providing favoring conditions for digestion. ***Control of the hydrogen ion concentration of saliva.*** It was noted earlier in our study that the reaction of whole saliva is normally maintained not far from neutral, between about cH $10^{-6.6}$ and $10^{-7.1}$ (pH 6.6–7.1).[2] Moreover, neither *acids* from foods or from bacterial action on food particles, nor *bases* from the use of sodium bicarbonate, or basic tooth pastes, or mouth washes, produce more than a slight variation from this reaction, and even then within a very short time after the entrance of such substances the reaction of the saliva again becomes normal.[3] Compounds which are responsible for maintaining this relatively constant hydrogen ion concentration are carbonates and phosphates that are always present in saliva. These compounds, acting as buffers, function in pairs: potassium hydrogen carbonate with carbonic acid, dipotassium hydrogen phosphate with potassium dihydrogen phosphate. Equations for reactions are as follows:

Buffer control of hydrogen ion/hydroxyl ion concentration of saliva

$$\textit{One pair of buffers}\begin{cases} KHCO_3 + H^+ \longrightarrow H_2CO_3 + K^+ \\ H_2CO_3 + OH^- + K^+ \longrightarrow KHCO_3 + HOH \end{cases}$$

$$\textit{The other pair of buffers}\begin{cases} K_2HPO_4 + H^+ \longrightarrow KH_2PO_4 + K^+ \\ KH_2PO_4 + OH^- + K^+ \longrightarrow K_2HPO_4 + HOH \end{cases}$$

This means that with both compounds present of either pair, one combines with sufficient hydrogen ions from invasions of acids, while the other combines with hydroxyl ions from moderate invasions of bases, so that the cH and cOH of the saliva are maintained within the fairly constant range specified. With even more than moderate additions of acids or bases, although the hydrogen ion and hydroxyl ion concentrations may be temporarily altered, they will presently be restored to the prevailing constant range through the same pairs of reactions.

This natural control of the hydrogen ion concentration of saliva within a range which is somewhat more on the acid than basic side of neutral is at variance with the notion that many people have that an acid reaction in the mouth is undesirable and that steps should be taken to bring about an alkaline condition. Such an idea is without scientific justification.

This maintenance of a relatively constant cH/cOH relationship in the saliva through reactions with these buffer compounds is of importance in relation to

[2] W. H. Howell, *Textbook of Physiology*, W. B. Saunders Company, 1937, p. 800; Starr, *J. Biol. Chem.*, **54**, 55 (1922); Clark and Henderson, *Ibid.*, **73**, 39 (1927), and Henderson and Millet, *Ibid.*, **75**, 559 (1927).

[3] Editorial, "A Biochemical View of Acid Mouth," *J. Am. Med. Assoc.*, **92**, 899 (1929).

dental hygiene since the hydrogen ion concentration of saliva is probably one of the factors which affects the deposit of tartar on teeth; tartar being largely a mixture of calcium phosphate and calcium carbonate the deposit of which is favored in a basic environment.

An aid in maintaining a favorable hydrogen ion concentration for salivary digestion. It will be recalled that the enzyme ptyalin is most active in the slightly acid environment of around cH 10^{-6} (p. 442). It therefore seems probable, not only that ptyalin meets with the optimum cH for catalyzing the hydrolysis of starch in the stomach but that, because of the presence of potassium hydrogen carbonate and dipotassium hydrogen phosphate in the food mass entering the stomach, this enzyme is able to continue its functioning in the stomach for a longer period than would otherwise be possible, due to the combination of these salts with the hydrogen ions of the penetrating hydrochloric acid, after the manner represented in the foregoing equations.

Salts in themselves favor salivary digestion. Furthermore, salts appear to favor the activity of ptyalin in some way other than through their buffer effect since it has been shown experimentally that with all other favoring conditions provided, save for the presence of salts, the activity of ptyalin is diminished.

Salts and gastric digestion. The puzzling question as to how hydrochloric acid is made for providing the relatively high concentrations of hydrogen ions, from about cH $10^{-1.2}$ to $10^{-3.5}$, for the optimum functioning of *pepsin* in catalyzing the hydrolysis of proteins has already been presented, likewise the theory that it may be made from reaction between the two salts, sodium chloride and sodium dihydrogen phosphate, which are always normally present within the blood (p. 445).

In intestinal digestion salts function in providing favoring hydrogen ion/hydroxyl ion concentrations. From the stomach the acid chyme is poured into the small intestine where salts, chiefly sodium bicarbonate, help to obtain the hydrogen ion/hydroxyl ion concentrations favorable to the activity of the various enzymes that catalyze reactions in this portion of the digestive tract (p. 455). Sodium bicarbonate is delivered into the duodenum from the liver, pancreas, and intestinal glands and becomes mixed with the intestinal contents where, through reactions with water, it is indirectly responsible for providing a supply of hydroxyl ions. These ions on coming into contact with hydrogen ions, for the most part provided by hydrochloric acid carried along from the stomach with the food mass, combine with them to make water, thereby

decreasing the hydrogen ion concentration in whatever locations this reaction occurs:

$$\underbrace{NaHCO_3}_{\substack{\text{From pancreas,}\\ \text{liver, and}\\ \text{intestine.}}} + HOH \longrightarrow NaOH + H_2CO_3$$

$$NaOH \downarrow \overbrace{Na^+ + OH^-}$$

$$+$$

$$\left.\begin{array}{l} H^+ \\ \downarrow \end{array}\right\} \text{from hydrochloric and other acids in intestinal contents.}$$

$$H_2O$$

But the mixing of the intestinal content takes place gradually, hence this decrease in hydrogen ion concentration takes place gradually, thus giving rise to considerable variation in cH in different parts of the digestive mass. In this way each enzyme stands an excellent chance of meeting somewhere along the intestinal tract with the specific hydrogen ion concentration that is favorable to its activity in the digestive process (p. 454).

The presence or absence of certain salts also seems to have an effect on the speed of enzyme action. For example, the presence of sodium chloride favors and perhaps is absolutely necessary to the action of pancreatic amylase. On the other hand the salts of heavy metals, notably silver and mercury salts and to a less degree copper, lead, and zinc salts, appear to have a toxic effect on digestive enzymes, thereby inhibiting their activity.

Ions provided by certain salts affect the contractility of muscle cells and the irritability of nerve cells. The relative concentrations of sodium, potassium, calcium, and magnesium salts in blood and in lymph that surrounds the cells has an *important effect on the contractility of muscle.* Sodium, potassium, and calcium ions are all essential for normal, rhythmic beating of the heart; sodium salts function to maintain normal osmotic pressure and are believed to have a specific function in relation to contractility of the cells. Potassium and calcium salts are antagonistic in action: an excess of potassium ions slows the heart beat by prolonging the period of relaxation, while a high concentration of calcium ions increases the strength of the contraction. Magnesium ions are also antagonistic to calcium ions in that they function to depress the heart muscle.

All four of these ions are *essential for the transmission of nerve impulse* in both the central and autonomic systems, but the mechanism by which they function is not understood. It has been observed, however, that excessively high concentrations of potas-

sium ions delay the transmission of nerve impulse. A decrease in calcium ion concentration below normal or an increase in magnesium ion concentration in the blood above normal acts as a depressant on the central nervous system affecting both sensory and motor nerves. Accordingly, with subnormal calcium ion concentration, symptoms indicative of nerve irritability occur such as excitability, muscle twitching, and tetany. This condition is treated sometimes by the administration of calcium salts to restore the calcium ion concentration of the blood to normal, sometimes by the administration of glandular preparations, since a disturbance in blood calcium is at times due to a disturbance of the parathyroid gland. An increase in the concentration of magnesium ions in the blood depresses the central nervous system, and in this connection it may be noted that magnesium sulfate is sometimes administered intravenously to produce an anesthetic effect.

Salts provide the necessary radicals for the building of bones and teeth. The cells of bones and teeth are subject to some mechanism whereby, normally, they are able to gather in from the blood stream nearly all of the calcium ions, the larger portion of the phosphate ions, and some of the carbonate ions. Indeed, 99 per cent of body calcium and 70 per cent of body phosphate are found in bones and teeth. Therefore, it follows, that within these cells the relatively high concentrations of these ions lead to extensive combinations of calcium ions with phosphate ions and with carbonate ions, accompanied by the precipitation of the relatively insoluble salts calcium phosphate (in larger proportion) and calcium carbonate (in smaller proportion), thereby providing the rigidity required of these tissues (Fig. 94). It also follows that, as a result of this mechanism, within the blood and lymph these ions are maintained in such low concentrations that their transportation to the cells can be accomplished without the precipitation of said salts in the conveying medium.

A study of salt structures within these cells has led to the finding that calcium phosphate and calcium carbonate are not laid down separately nor in haphazard manner, but rather that they are mutually assembled in a definite crystalline pattern.

Just what the mechanism is which controls the gathering-in of these ions, especially calcium and phosphate ions, on the part of the cells of bones and teeth, and which provides for the maintenance of not too high (to guard against precipitation) but nonetheless adequate concentrations of these ions in the blood, for the continuous needs of these tissues, is not entirely known. But

it is known that the deposition of calcium and phosphate salts in teeth and bones are affected both by the secretion of a hormone produced in the parathyroid glands and by the supply of vitamin D (calciferol) within the body. This hormone functions to regulate the concentrations of calcium and phosphate ions in blood and

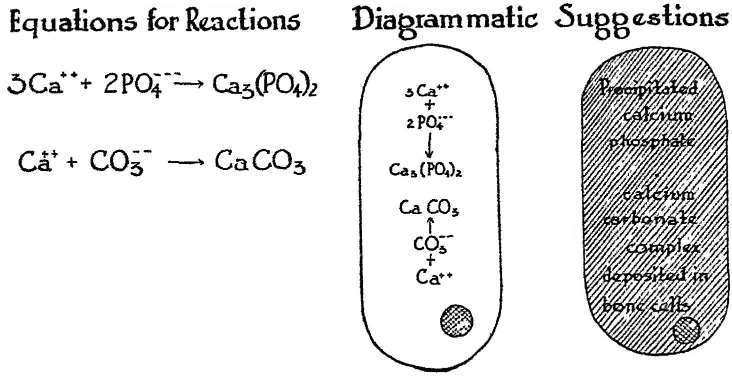


FIG. 94. Calcium, phosphate, and carbonate ions contribute to the making of insoluble salts in the cells of bones and teeth.

lymph; vitamin D is believed to function both by increasing absorption of calcium and phosphate ions from the intestine and by favoring the deposit of calcium phosphate of long bones. Sherman suggests that, with an abundance of calcium and phosphate provided in the diet and a liberal supply of vitamin D, superior height and erectness of carriage may result.[4]

The deposit of these salts in the cells of osseous tissue goes on most rapidly during the period of growth but it is by no means confined to this period. An interchange of salt radicals is known to occur continuously during the life of the individual between the bone cells and the blood, but this interchange takes place very slowly.

During pregnancy and the lactation period, if there is an inadequate concentration of calcium or phosphate ions in the blood, either because of their insufficiency in the food or because of a lack of vitamin D, some of the salts stored in the bones of the mother may be drawn upon to meet the demands of the growing organism. For this reason, during this period, the diet of the mother should be replete with calcium, phosphate, and vitamin D.

Iron and copper salts function in building hemoglobin. Although the total amount of iron contributing to the compounds in the

[4] H. C. Sherman, *Chemistry of Food and Nutrition*, The Macmillan Company, 1941, pp. 433–434.

human body is relatively very small, about one part in 25,000 parts of body weight, iron is undoubtedly one of the very important elements physiologically. The greater part of this element is present in the hemoglobin of red blood cells, but it is also widely distributed in other locations throughout the body in that it is a constituent of chromatin which is found in the nucleus of every living cell. And within recent years there has been a growing realization on the part of physiological chemists that in some way, not yet well understood, these iron-containing compounds of chromatin have a fundamental influence on the reduction-oxidation reactions which are of such vital importance in living cells.

A more or less constant destruction of red blood cells goes on constantly in the body with the elimination of iron compounds, chiefly by way of the intestine. This makes it necessary that a supply of available iron — from 8–12 milligrams daily [5] — should be continuously provided by components of the food mass to make up for that which is eliminated. Formerly it was quite generally agreed that the body could utilize this iron from organic compounds but probably not from inorganic salts. But of recent years, clinical experience with the treatment of certain types of anemia has demonstrated that the administration of ferrous carbonate, ferric chloride, and other inorganic iron salts is followed by a marked increase in the hemoglobin of the blood. Of these salts some authorities believe that the ferrous salts are more readily utilizable than the ferric salts, but this is not yet definitely known. As for the complex organic compounds of iron such as hematin, it has been experimentally established that, when used as foods, they are not utilized appreciably, perhaps because they cannot pass through the intestinal membrane. Hence, it is claimed by some that such complex iron compounds must undergo digestive reactions to make simple iron salts before they can be absorbed and utilized.[6]

It has also been learned that hemoglobin building goes on more rapidly when a trace of copper salts is present along with the iron salts, and it is believed that they function as catalysts to speed up some essential reactions involved. But although copper salts are thus essential, they are adequately provided by the usual diet and do not require any special dietary consideration. It is also known that there is better utilization of iron salts if calcium ions are provided in abundance.

[5] H. C. Sherman, *Chemistry of Food and Nutrition*, The Macmillan Company, 1941, p. 288.

[6] C. A. Elvehjem, "The Relative Value of Inorganic and Organic Iron in Hemoglobin Formation," *J. Am. Med. Assoc.*, **98**, 1047 (1932); also Elvehjem, Hart, and Sherman, "The Availability of Iron from Different Sources for Hemoglobin Formation," *J. Biol. Chem.*, **103**, 61.

Calcium ions are essential to the clotting of blood. The clotting of blood involves the making of an insoluble fibrin from fibrinogen — a globulin which is present in colloidal solution in the blood stream. Calcium ions and blood platelets are known to play essential parts in this clotting process; but just how the clot is formed is unknown, although various theories have been advanced to explain the phenomenon, nor why it occurs in injured tissue but does not normally take place in the circulating blood. We shall follow the theory offered by the physiologist, Howell, and note how the calcium ions supposedly function in the process.

This theory supposes that fibrinogen, calcium salts, and prothrombin, which are present in the circulating blood, are all necessary to the clotting process. Another substance is also present: namely, heparin, whose function is believed to be that of inhibiting the action of prothrombin, to make thrombin, the latter being essential in the clotting mechanism. But when tissue injury occurs some of the blood platelets disintegrate to make a thermoplastic substance which inactivates heparin, thereby leaving the prothrombin free to enter into the reactions responsible for clotting. As a result, prothrombin then reacts with calcium ions to make thrombin, which in turn reacts with the fibrinogen to make the insoluble fibrin.

In circulating blood

Fibrinogen
Calcium salts
Prothrombin $\xleftarrow{\text{inhibits activity of}}$ Heparin

In tissue injury

A thermoplastic substance made $\xrightarrow{\text{inactivates}}$ Heparin

Blood clot forms

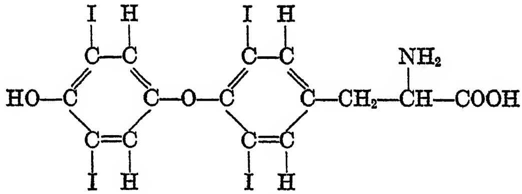
Prothrombin + Calcium salts → Thrombin
Thrombin + Fibrinogin → Fibrin, an insoluble substance which entangles blood cells and forms the clot.

It is because calcium ions are essential to this process that they are usually removed from the blood that is to be administered by indirect transfusion, a treatment in which it is important that the blood so used should not be capable of clotting. This removal is accomplished by mixing sodium citrate with the blood taken from the donor, the calcium being thereby precipitated in the relatively insoluble calcium citrate:

$$Ca^{++} + 2\,Na_2C_6H_5O_6 \rightarrow \downarrow Ca(C_6H_5O_6)_2 + 2\,Na^+$$

Iodides are used by the cells of the thyroid gland for building thyroxine. Ever since ancient times people in various sections of the earth have made use of marine products for relief from goiter. Then around 1850 Professor Chalin of Paris, after having made a study of goiter in France, announced his conclusion that there must be a relationship between this affliction and iodine; since he found that in locations in which the air, soil, and water were rich in iodine salts, goiter was unknown. Little heed, however, was given to these findings and to this belief of Professor Chalin. But many years later, in 1896, a scientist by the name of Baumann reported the actual discovery of iodine element in the material of the thyroid gland, and in 1914 Dr. Kendall of the Mayo Clinic isolated crystals of an iodine-containing compound from thyroid tissue to which he gave the name *thyroxine* and which he found to be the active principle of this gland.

This substance *thyroxine* had been proved to be a derivative of the amino acid tyrosine and the composition of its molecule is believed to be as represented by the following structural formula:



Thyroxine

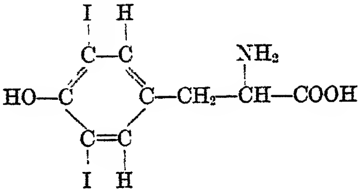
Thyroxine occurs combined with protein in the thyroid gland in the complex known as thyroglobin. It has the specific power of stimulating metabolism. Kendall claims that any increase in the basal metabolism which may extend over a period of two or three weeks or longer can be due to no other cause than an increase over the normal secretion of this important compound. The fact that this secretion increases metabolic reactions throughout the body indicates that all body activities are influenced by the functioning, normally or otherwise, of the thyroid gland. After an extensive study of thyroxine Kendall wrote thus of its physiological importance:

"The chemical investigation of thyroxine has been of more than passing interest because of the knowledge that one of the most significant secrets of biology is bound within its molecule. This single substance can transform flesh and blood from a mass of protoplasm into a rational human being."[7]

More recently, another iodine-containing compound, likewise a derivative of tyrosine, *3,5 diiodotyrosine* has been isolated from the thyroid gland. This substance has some of the physiological effects of thyroxine but does not

[7] E. C. Kendall, *Thyroxine*, 1929, p. 230. By permission of Chemical Catalogue Co., publishers.

stimulate metabolism as does thyroxine and it has been suggested that it may be a precursor of the latter compound:



The structural formula for the molecule of *3,5 diiodotyrosine*. Note its resemblance to that of thyroxine.

For the building of this essential substance, thyroxine, it is believed that the thyroid gland makes use of iodides provided by the food and water supply. Certainly there is a striking relationship between the incidence of simple goiter and the geographic distribution of iodide salts. In areas remote from the sea, or in mountainous regions, where the soil, hence the vegetation and water supply, are deficient in iodine salts the so-called "simple or endemic goiter" is of common occurrence.

In 1917 an experiment, now considered as classic, was conducted by Marine in Akron, Ohio, a city situated in a goiter belt. Sodium iodide was administered to a large group of school children as a prophylactic for simple goiter. Reporting on the results of this experiment four years later, Marine noted that of the 2190 children who had taken sodium iodide only five developed goiter, whereas of the 2305 children not taking the iodide 495 had developed goiter. The value of similar prophylactic doses has since been demonstrated in Switzerland and in other goiter belts. Indeed, so striking is the relationship between the iodide supply and the incidence of simple goiter that, although other factors may enter into the situation, it is considered that deficiency of iodine is the predominating factor.

The small amount of iodide actually required normally by the body (estimated at about 0.000014 gram of iodide per day) is amply provided for by the food and water supply in most regions. But in regions where there is a deficiency in iodine compounds, various means have come to be employed to augment these compounds, chiefly through the use of iodized salts. This protective measure may well be regarded in the nature of supplying a deficiency rather than as medication and it is a practice which has come to receive the support of the medical profession.

In the face of the above findings it should not be surprising to learn that iodides (also Lugol's solution, which is iodine dissolved in potassium iodide) have come to be used therapeutically in the

treatment of certain types of goiter. However, iodides should not be regarded as a panacea for all goiter conditions, since there are certain types of thyroid disturbance in which iodine medication appears to be definitely harmful. In any event, iodides should never be administered in pathological conditions save under the direction and supervision of a competent physician.

Certain salts function as "buffers" in maintaining the normal cH/cOH relationship in the blood, lymph, and cells. One of the very striking phenomena in the human body is the fairly constant hydrogen ion/hydroxyl ion concentration range that is maintained in health in the blood, lymph, and cells despite the absorption from the intestine of variable quantities of acids and bases; the entrance into the blood from the cells of variable quantities of strong and weak acids; and the continuous presence of salts of strong bases and weak acids (p. 502).

This hydrogen ion/hydroxyl ion relationship in the *blood and lymph* is kept within the limited range, always slightly on the basic side, of from cH $10^{-7.3}$ to cH $10^{-7.5}$; whereas in the *actively functioning cells* the range is maintained within limits of from slightly on the basic side, as in the blood and lymph, to a reported cH of $10^{-5.6}$, or somewhat on the acid side of neutral.[8] In disease the absolute limits possible to the living body that have been reported for the blood and lymph are cH 10^{-7}, as in a condition of extreme acidosis, and cH $10^{-7.8}$ as in extreme alkalosis.

Pairs of buffer substances and their functioning. In the presence of the need to protect itself from the overrunning of this cH/cOH relationship beyond the healthy normal limits, nature has established several control mechanisms, one of which is through the agency of pairs of buffers, either salts with salts, or salts with weak acids. Such a buffer system, whether within the body or in solutions outside of the body, is capable of preventing marked fluctuations in hydrogen ion/hydroxyl ion concentrations upon the addition, within limits, of either acids or bases. This is in marked contrast with just water or with unbuffered solutions which undergo appreciable increases in cH when acids are added and in cOH when bases are added.

The buffer salts provided in the blood, lymph, and cells are chiefly bicarbonates, mono and dihydrogen phosphates, and proteinates of sodium and potassium — the sodium salts predominating in the blood and lymph, and the potassium salts predominating

[8] Peyton Rous, "The Relative Reaction of Living Mammalian Tissues," *Science*, **60**, 363 (1924).

Some of the sources of acids and bases, hence of hydrogen ions and hydroxyl ions, in the blood and lymph

	In Blood and Lymph		*From cells*	
		Carbonic acid ← (weak but in large quantities)	← Carbon dioxide + Water	From the metabolism of carbohydrates, fats, and proteins.
		Lactic acid ←	←	
From food mass of the average diet and *absorbed from the intestine*, such acids as:				
→	Acetic acid (All weak)			
→	Lactic acid (All weak)			
→	Citric acid (All weak)	Phosphoric acid ← (weak)	←	From metabolism of proteins.
→	Fatty acids (All weak)	Sulfuric acid ← (strong but in small quantities)	←	
From fruits and other foods, salts such as:				
Potassium tartrate + Water →	Tartaric acid (weak) + Potassium hydroxide (strong)			
Potassium citrate + Water →	Citric acid (weak) + Potassium hydroxide (strong)			
Sodium bicarbonate + Water →	Carbonic acid (weak) + Sodium hydroxide (strong)			
	Hydrochloric acid (strong but in small quantities)			

in the cells. The buffer acids provided are carbonic acid and hydrogen proteinates (meaning proteins in their acid capacity). The buffer substances are paired as follows:

Buffer pairs chiefly in blood and lymph		*Buffer pairs chiefly in cells*	
Sodium monohydrogen phosphate	Na_2HPO_4	Potassium monohydrogen phosphate	K_2HPO_4
Sodium dihydrogen phosphate	NaH_2PO_4	Potassium dihydrogen phosphate	KH_2PO_4
Sodium bicarbonate	$NaHCO_3$	Potassium bicarbonate	$KHCO_3$
Hydrogen carbonate	H_2CO_3	Hydrogen carbonate	H_2CO_3
Sodium proteinate		Potassium proteinate	
Hydrogen proteinate		Hydrogen proteinate	

The following equations represent reactions through which these three buffer pairs function *in the blood and lymph* to prevent an undue increase in the concentration of either hydrogen ions or hydroxyl ions in these locations:

In the blood and lymph, *for removal of hydrogen ions and hydroxyl ions in excess of normal concentrations*

Phosphate pair of buffers

$$Na_2HPO_4 + H^+ \longrightarrow NaH_2PO_4 + Na^+$$
$$NaH_2PO_4 + OH^- + Na^+ \longrightarrow Na_2HPO_4 + HOH$$

Carbonate pair of buffers

$$NaHCO_3 + H^+ \longrightarrow H_2CO_3 + Na^+$$
$$H_2CO_3 + OH^- + Na^+ \longrightarrow NaHCO_3 + HOH$$

Protein pair of buffers [9]

$$\text{Sodium proteinate} + H^+ \longrightarrow \text{Hydrogen proteinate} + Na^+$$
$$\text{Hydrogen proteinate} + OH^- + Na^+ \longrightarrow \text{Sodium proteinate} + HOH$$

The protective reactions of buffer substances *in the cells,* in both the tissue cells and red blood cells, are identical with those represented above save that *potassium salts* are chiefly involved instead of sodium salts. In all three locations — blood, lymph, and cells — the proteins, because of their comparative abundance, are the most important hydrogen ion control agents through buffer action. In this respect the *hemoglobin salts* of the red blood cells are particularly efficient.

Various factors influence the effectiveness of these salt/salt and salt/acid buffer systems; among these factors are the relative concentrations of the buffer pairs themselves, and the hydrogen ion concentration of the medium. This latter factor we shall not attempt to discuss, but it is interesting to learn that the buffer

[9] Also see the discussion of the amphoteric nature of proteins, pp. 424–425.

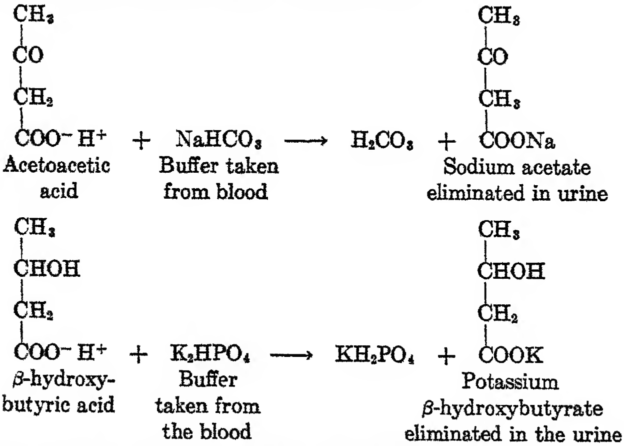
action of the sodium bicarbonate/hydrogen carbonate pair is at its greatest efficiency when the hydrogen ion concentration of the blood is within the normal range (cH $10^{-7.3}$–$10^{-7.5}$); whereas the pair of phosphate salts becomes most effective[10] as the hydrogen ion concentration approaches the dangerous neutral extreme of cH 10^{-7}.

Pathologically. Any marked variations away from the normal cH/cOH within the blood is indicative of a serious disturbance of the acid-base equilibrium therein. Moreover, regardless of the location of the disturbing factor, the disturbance as a whole presently becomes systemic in its extent.

Acidosis. Should the hydrogen ion concentration of the blood reach values greater than cH $10^{-7.3}$ (cOH $10^{-6.7}$), although still on the basic side of neutral, a condition known as *acidosis* prevails. This condition is due to the presence in the blood of excessive quantities of acids, other than carbonic acid. It is such an excess of acids that is responsible for the acidosis that frequently accompanies either severe diabetes or starvation when, due to a disturbance in the normal metabolism of glucose and fats, an accumulation of *acetoacetic acid* (diacetic acid) and *beta-hydroxybutyric acid* occurs in the circulating fluids.

And as should be expected, an increase in hydrogen ion concentration above normal in the blood, which follows upon the persistent appearance of these acids, is preceded and accompanied by an abnormal demand upon the hydrogen ion concentration control buffers, especially sodium bicarbonate although the relatively small quantities of potassium salt functions also and in like manner:

Removal of acid-controlling buffers during acidosis



[10] Meyer Bodansky, *Introduction to Physiological Chemistry,* 1938, p. 262.

As a direct result of this demand, the concentration of "base-making salts" in the blood becomes considerably decreased below normal — a condition which the physiologist sometimes refers to as "a decrease in the alkali reserve of the blood" — and the resulting salt products which are eliminated by the kidneys rise above their normal concentrations in the urine.

Alkalosis. On the other hand, any decrease in hydrogen ion concentration below the normal limit (cH $10^{-7.5}$) means, of course, an increase in hydroxyl ion concentration above the normal limit (cOH $10^{-6.5}$) and is known as *alkalosis.* Such a condition may be brought about by copious vomiting accompanied by a carrying out of considerable hydrochloric acid from the system, or it can be produced by excessive administration of base-producing salts such as sodium bicarbonate. This condition, although of less frequent occurrence than that of acidosis, gives rise to an abnormal demand upon the hydroxyl ion control buffers, a demand which must continue as long as the condition prevails.

Salts function in reversible reactions to produce conditions favorable both for transportation of oxygen and carbon dioxide in the blood and for their exchange at cells and lungs. Closely allied to the buffer action of salts is their functioning through various reactions as respiration control factors. *At the cells,* through this agency, certain conditions are obtained (1) which promote the decomposition of oxyhemoglobin whereby oxygen is released to the cells for cell oxidative needs and (2) which take care of the considerable quantities of carbon dioxide made, by favoring the reactions for its combination to make bicarbonates for transportation to the lungs. *At the lungs,* again in part through the agency of reactions involving salts, conditions are obtained which favor (1) the delivery of carbon dioxide by bringing about the decomposition of the above mentioned bicarbonates, and (2) the picking up of oxygen by hemoglobin for transportation to the cells. Some details as to how these phenomena are accomplished are considered in the following.

At the active cells. *What happens to carbon dioxide.* In all active cells oxygen is continuously being requisitioned for reaction with partner substances made from glucose, fats, and proteins in the processes of cell metabolism, and at the same time carbon dioxide and water are continuously being made. This results in a higher concentration of carbon dioxide in the cells than in the surrounding lymph and blood, and a consequent continuous diffusion of carbon dioxide from the cells into the lymph and thence to the

blood. Some of this carbon dioxide can be carried away as such in solution but by far the major portion of it reacts with water to make carbonic acid,[11] and the red blood cells provide a catalyst, carbonic anhydrase, which favors this reaction:

$$CO_2 + H_2O \xrightarrow{\text{carbonic anhydrase}} H_2CO_3$$

This continual pouring of carbonic acid into the lymph, blood plasma, and red blood cells results in the favoring of reactions between this acid and salts in these locations in the direction of the making of bicarbonates, chiefly sodium bicarbonate in the lymph and plasma, and chiefly potassium bicarbonate in the red blood cells.

Disposal of carbonic acid made at the cells

In lymph and blood plasma

$$H_2CO_3 + NaCl \rightleftarrows NaHCO_3 + HCl$$

$$H_2CO_3 + \text{Na proteinate} \rightleftarrows NaHCO_3 + \text{H proteinate}$$

In red blood cells

$$H_2CO_3 + K_2HPO_4 \rightleftarrows KHCO_3 + KH_2PO_4$$

$$H_2CO_3 + KHb \rightleftarrows KHCO_3 + HHb$$ [12]

Condition favoring decomposition of oxyhemoglobin. It is due to these reactions, in which bicarbonates are made at the expense of carbonic acid, that the blood is able to dispose of the large quantities of carbon dioxide made in the cells throughout the body without a marked increase in the concentration of hydrogen ions in the locations concerned.

However, even with this mechanism, venous blood laden with carbon dioxide does acquire a slightly higher hydrogen ion concentration than that of the arterial blood. And it is this slightly higher hydrogen ion concentration which provides one of the favoring conditions for the decomposition of oxyhemoglobin, this compound becoming less stable as the cH of the medium increases:

$$\text{Oxyhemoglobin} \rightarrow \text{Oxygen} + \text{Hemoglobin}$$

This facilitates the escape of oxygen to the plasma, thence to the lymph, and to the functioning cells which must have it for participation in reactions essential to living (Fig. 95).

[11] It is claimed that a portion of the carbon dioxide (about 10 per cent) is carried by the hemoglobin through combination at the amino group ($HbNH_2 + CO_2 \rightarrow HbNHCOOH$) and that this compound, being unstable, decomposes at the lungs. F. J. W. Roughton, "Recent Work on Carbon Dioxide Transport by the Blood," *Physiological Review*, **15**, 241 (1935).

[12] Hb is the customary abbreviation for hemoglobin, HHb represents hemoglobin as an acid, KHb represents the potassium salt of hemoglobin. Both are present in red blood cells.

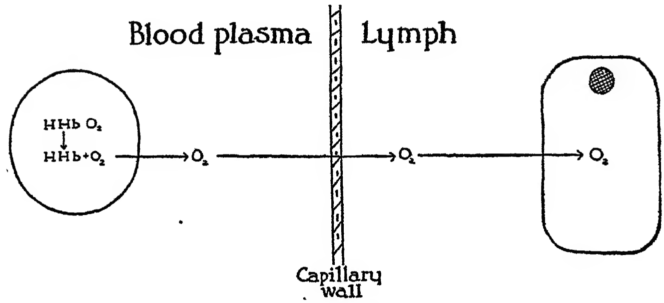


FIG. 95. Oxygen Taken by the Cells from Oxyhemoglobin for Use in Metabolic Reactions

At the lungs. In this location we find that the two living needs, (1) delivery of carbon dioxide through the decomposition of bicarbonates and (2) picking up of oxygen by the hemoglobin, are mutually helpful in that one process aids in providing favoring conditions for the other.

The concentration of *carbon dioxide* in the blood which reaches the lungs is continuously greater than that in the air entering the alveoli of the lungs; consequently there is an unceasing escape of carbon dioxide from the blood to the outside air. At the same time the concentration of oxygen entering the lungs being greater than that within the blood stream, there is a continuous passing of *oxygen* from the air into the blood where it meets hemoglobin returned from the active cells and combines with it to make oxyhemoglobin (Fig. 96).

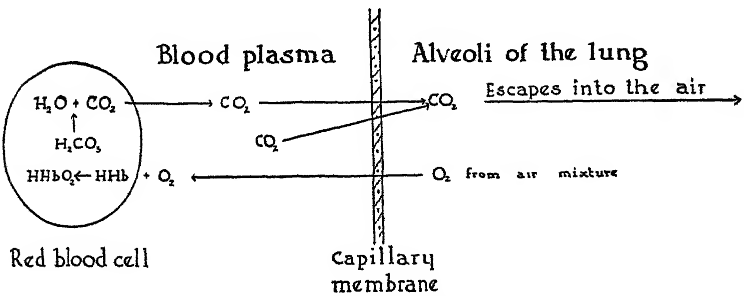


FIG. 96. The Exchange of Oxygen and Carbon Dioxide at the Lungs

This oxyhemoglobin being a stronger acid than hemoglobin, a condition is obtained which favors its reaction with potassium bicarbonate in the red blood cells to make more carbonic acid.

Then, there being a way out for carbon dioxide, the carbonic acid thus made decomposes to make carbon dioxide and water.

$$\begin{array}{ll} HHbO_2 + KHCO_3 \rightleftarrows KHbO_2 + & H_2CO_3 \\ & \big\downarrow \text{Carbonic anhydrase (catalyst)} \\ & H_2O + CO_2 \xrightarrow[\text{removed at lungs}]{} \end{array}$$

These reactions are favored both by the constant removal of carbon dioxide through the alveoli and by the presence of the catalyst carbonic anhydrase, provided in the red blood cells, which now favors the reaction in the opposite direction from that which it favored at the cells.

The enzyme carbonic anhydrase is present in red blood corpuscles but not in the plasma. It is therefore believed that the decomposition of carbonic acid takes place largely *within the red blood cells* rather than in the plasma. As the carbonic acid within these cells is removed, due to its continual decomposition and the escape of carbon dioxide, more carbonic acid is drawn into the cells from the plasma. At the same time hydrochloric acid moves from the

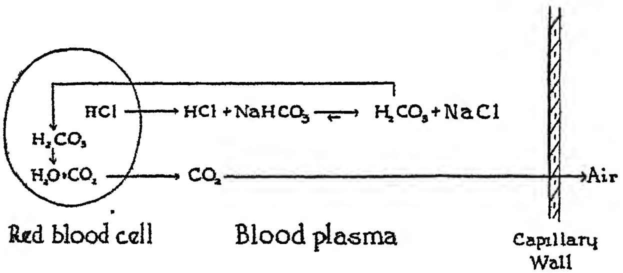


Fig. 97. At the lungs a continuous decomposition of carbonic acid takes place within the red blood cells (where a favoring catalyst is provided toward this end).

cells to the plasma, where it reacts with sodium bicarbonate to make more carbonic acid and sodium chloride, as is suggested by the accompanying diagram (Fig. 97). The slightly lower hydrogen ion concentration produced in the blood, chiefly by the decrease of the concentration of hydrochloric acid in this region, is favorable to the combination of oxygen with hemoglobin to make oxyhemoglobin.

Selective reabsorption and elimination of salts by the kidneys. Elimination of salts from the body is accomplished, in the main, by the kidneys. To a less degree they are also excreted by the skin, and certain salts (p. 459) are eliminated chiefly in the feces. It will be recalled (p. 491) that two sources of the salts of the blood are as follows: (1) they are provided in the food mass and absorbed into the blood from the digestive tract, (2) they are made at the

cells from acid products of metabolism — such as carbonic acid, lactic acid, sulfuric acid, and phosphoric acid — through reactions with bases and salts, including buffer salts. Because of the latter reactions it follows that should acids enter the blood stream in considerable quantities, either from the digestive tract or from the cells, the proportion of such buffer salts of the blood as are needed for reactions with acids would in time become depleted, unless some means were provided for their conservation. On the contrary should bases enter the blood in considerable quantities — although of less frequent occurrence than is true of acids — the proportion of base-controlling buffer salts would become depleted without the provision of a control mechanism.

An aid to maintaining the normal concentration of buffer salts in the blood. And it is at the kidneys through the agency of certain favored reactions, accompanied by (1) *the selective reabsorption of such buffer salts as are needed at the time, and* (2) *the elimination of others,* that the concentrations and proportions of these salts are maintained in the blood within required limits. In so doing the kidneys perform their own important part in the mechanism whereby nature maintains the constant and limited hydrogen ion concentration range within the blood which is essential to life and health.

It is believed that salts filter through the glomeruli of the kidneys in about the same concentrations as they occur in the plasma of the blood; but that certain reactions take place in the renal tubules whereby the relative concentrations of various salts are altered, with sodium and potassium salts either excreted in the urine or reabsorbed into the blood as a control device toward the maintenance of their needed relative concentrations within the blood (Fig. 98).

The chief mechanism. The principal mechanism whereby this control is effected is through the agency of reversible reactions involving buffer salts, chiefly the phosphate salts, sometimes the reaction in one direction being favored, sometimes the reaction in the other direction, depending upon which salt is destined for the major absorption.[13] Both disodium hydrogen phosphate (Na_2HPO_4) and sodium dihydrogen phosphate (NaH_2PO_4) salts are brought to the kidneys in the blood and both are excreted from the kidneys in the urine. But whereas in the blood the disodium hydrogen phosphate predominates, in the urine — under normal

[13] Although both sodium and potassium salts are present in the blood the sodium salts are greatly in predominance, hence to avoid confusion, the discussion is, in the main, in terms of the sodium salts.

conditions of metabolism and on an ordinary mixed diet — the concentration relationship is reversed and sodium dihydrogen phosphate predominates. As a consequence, *while the reaction of*

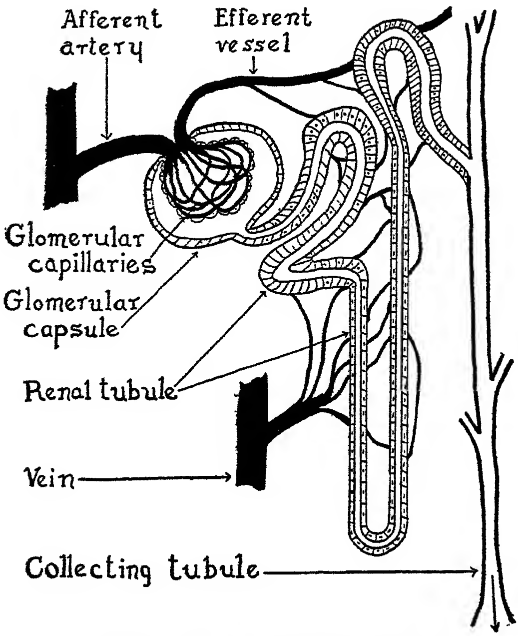


FIG. 98. Diagram of Kidney Unit

The *glomerular capsule* — where water, salts, urea, and other components of the blood plasma are believed to enter by filtration from the glomerular capillaries. The *renal tubule* — where changes in the relative concentrations of various salts are believed to take place as the reabsorption of components that are needed by the blood occurs. The *collecting tubule* — through which the urine finds exit from the kidney unit.

the blood in this and other regions *is maintained slightly on the basic side, that of the urine is usually more acid than the blood* from which it is secreted.[14]

In the blood brought to the kidneys (about pH 7.4)	In the urine as excreted (commonly about pH 6)
$Na_2HPO_4 : NaH_2PO_4 :: 4 : 1$	$Na_2HPO_4 : NaH_2PO_4 :: 1 : 9$

This difference in the *normal* relative concentrations between these buffer salts in the blood and urine is brought about by reactions

[14] Disodium hydrogen phosphate on hydrolysis results in a solution which is basic in reaction; whereas sodium dihydrogen phosphate results in a solution which is acid in reaction.

and accompanying reabsorptions at the cells of the renal tubules, as represented in the following:

$Na_2HPO_4 + H_2CO_3 \rightleftarrows$	NaH_2PO_4	$+$	$NaHCO_3$
Brought to the kidney cells by the blood	A more acid salt, which is excreted by the kidneys		Reabsorbed by the blood, thereby maintaining a relatively high concentration of this base-producing buffer in the blood

When greater than usual quantities of acids enter the blood, as may be the case when certain acids are provided in large quantities in the food mass or when there is a disturbance in the glucose/fat metabolism (p. 473), excessive demands are made upon the acid-controlling buffer salts, hence the need for their greater than normal reabsorption from the kidney, in which event the making of the dihydrogen phosphate salts is favored to an even greater degree than that indicated in the foregoing. As a result a proportionately greater quantity of this salt appears in the urine, and as a consequence the hydrogen ion concentration of this excretion is above the usual value, sometimes as high a value as pH 4.8.

On the other hand (1) *if the concentration of acids in the blood stream is decreased below the average value,* as occurs temporarily when during gastric activity hydrochloric acid is being secreted or when persistent vomiting occurs; or (2) *if the concentration of base-making salts in the blood is increased* above average, as is the case when organic sodium and potassium salts in the food mass are high (as on a diet rich in fruits and vegetables), or when a large amount of such a salt as sodium bicarbonate is taken medicinally — if either of the above conditions is obtained, then the normal concentration of sodium bicarbonate in the blood can be maintained without the reabsorption of so much of this salt from the kidneys. In this event the reaction which favors the making of sodium dihydrogen phosphate and sodium bicarbonate is checked, or even reversed; if the latter, then more than the usual quantity of the disodium phosphate appears in the urine. When this occurs the reaction of the urine is more toward the basic end of the range.

$NaH_2PO_4 + NaHCO_3 \rightleftarrows$	Na_2HPO_4	$+$	H_2CO_3
	Excreted in the urine		Reabsorbed or excreted

Another control mechanism. A second important regulatory mechanism which operates at the kidneys to conserve the normal

concentrations of sodium and potassium salts in the blood, especially when acidosis threatens, is the *making of ammonia in the kidneys*, possibly from urea brought to these organs for excretion, possibly by deaminization of certain amino acids by the kidney cells. This ammonia then enters into various reactions, accompanied by a selective absorption, whereby the concentration of ammonium salts in the urine is increased, and sodium and potassium salts are retained in the blood. The following is suggestive as to what may possibly occur:

Base making salts returned to blood

Made in kidneys — Brought by blood

$$\begin{array}{l}
\overbrace{2\,NH_3}^{\text{Made in kidneys}} + \overbrace{2\,H_2CO_3 + Na_2SO_4}^{\text{Brought by blood}} \longrightarrow (NH_4)_2SO_4 \;\big|\; + 2\,NaHCO_3 \\
NH_3 + H_2CO_3 + NaCl \longrightarrow NH_4Cl \;\big|\; + NaHCO_3
\end{array}$$

Excreted in urine

But should the concentrations of sodium and potassium salts in the blood be in excess of body needs, the production of ammonia and ammonium salts at the kidneys is not stimulated, in which case sodium and potassium salts, including even sodium bicarbonate, are sent on in the urine where they appear in greater than usual quantities.

As a result of the operation of these varied control mechanisms the reaction of normal urine, although most commonly about pH 6, can vary considerably from time to time, the limits having been reported as from pH 4.8 to about pH 8.4.[15]

The excretion of sodium chloride. Sodium chloride is unique in that it is the one salt that is commonly and deliberately added to the diet. It is also the salt that is excreted in largest quantity at the kidneys. Associated with these two facts is another of significance: namely, the body maintains a relatively constant concentration of sodium chloride in blood and lymph thus insuring the necessary osmotic pressure at the cells. The regulation of the concentration of this salt in the extracellular fluids is chiefly the work of the kidneys; hence sodium chloride taken in with the food in excess of physiological needs is promptly excreted. In a so-called "salt free" diet, that is, one in which no extra sodium chloride has been added either in food preparation or as a condiment, the elimination of this salt in the urine drops to a minimum.

Sodium chloride is also excreted at the skin, but ordinarily not in large amounts. However, when sweating is excessive as in hot

[15] H. C. Sherman, *Chemistry of Food and Nutrition*, 1941, p. 242.

weather or during strenuous labor, considerable quantities of this salt solution are thus removed from the system. Under these conditions, well salted broth or consomme may be a more refreshing drink than water alone, since either would aid in restoring normal salt concentration in body fluids.

Salts commonly excreted in the urine. It follows from the foregoing discussion that the salts in normal urine may vary considerably both as to the particular salts and to their relative quantities. However, the following salts are usually present in larger or smaller quantities.

Inorganic salts

$$\left.\begin{array}{l}\text{Sodium}\\ \text{Potassium}\\ \text{Ammonium}\end{array}\right\}\text{ with }\left\{\begin{array}{l}\left.\begin{array}{l}\text{chloride}\\ \text{dihydrogen phosphate}\\ \text{monohydrogen phosphate}\\ \text{sulfate}\end{array}\right\}\text{ in predominance}\\ \text{carbonate (in urine of more basic reaction)}\end{array}\right.$$

$$\left.\begin{array}{l}\text{Calcium}\\ \text{Magnesium}\\ \text{Iron}\end{array}\right\}\text{ salts in traces, being eliminated chiefly in the feces.}$$

$$\textit{Organic salts}\left\{\begin{array}{l}\text{urates (always present)}\\ \left.\begin{array}{l}\text{oxalates}\\ \text{citrates}\\ \text{lactates}\end{array}\right\}\text{ in larger amounts when the urine is more basic}\end{array}\right.$$

Questions

1. The normal reaction of whole saliva is about pH 6.6–7.1, and the entrance of neither acids nor bases into the mouth produces more than a slight temporary variation from this value.
   a. What information does the expression pH 6.6 to 7.1 provide concerning conditions within the normal saliva? Interpret as fully as you can.
   b. What components of normal saliva are responsible, in the main, for the constancy of this value?
   c. If an acid enters the mouth what reactions could be expected to set in to maintain this relatively constant pH condition? Represent by equations.
   d. If an alkaline mouth wash is used, what reactions might be set up to maintain the normal pH? Again, represent by equations.

2. Name four important physiological functions of calcium salts and their ions. Indicate by word equation (where possible) any reaction which is believed to be involved in these functions. What are the chief food sources of these essential calcium salts?

3. Where is the element iron found within body cells? With what two physiological functions are iron compounds associated? What are the chief sources of these salts in the diet? About how much iron element is needed daily?

4. To what physiologically important compound is iodine an essential element? Of what amino acid is this compound an iodine derivative? What is the function of this iodine containing compound? What is the chief food source of iodine? How much iodine element must be supplied daily to meet the normal individual requirement?

5. The blood and lymph are highly buffered solutions capable of maintaining a relatively constant hydrogen ion concentration.

a. What is meant by the expression "buffered solutions"? Name three pairs of buffer substances found in these fluids.

b. Mention two acids which normally enter the lymph and blood as metabolic end products. Indicate by means of equations the manner of reaction on the part of functioning buffers with each of these acids.

c. Cite one source from which a base enters the lymph and blood. Indicate by the use of equations the resulting reactions with one functioning buffer.

d. What is the reported normal cH range within the blood and lymph that is consistent with health?

e. How does the removal of carbon dioxide at the lungs affect the hydrogen ion concentration of the blood and lymph?

6. Follow the processes involved in the transportation of oxygen from the air sacs of the lungs to the actively functioning cells, indicating:

a. The conditions at the lungs that favor its entrance into the blood stream.

b. The reactions involved in providing for its combination with hemoglobin.

c. The conditions at the cells that favor the decomposition of oxyhemoglobin and the entrance of oxygen to the functioning cells.

7. Follow the processes involved in the passage of carbon dioxide from the cells where it is made to its escape at the lungs, indicating:

a. The conditions at the cells favorable to the entrance of carbon dioxide into the blood and lymph.

b. Nature's provisions for its transportation in the circulating fluids, indicating reactions concerned.

c. Reactions at the lungs that result in the remaking of carbon dioxide and conditions there encountered which favor its escape to the air.

8. What salts are commonly excreted by the kidneys? Which of these salts are in the main absorbed directly from the food mass? Which are made in the processes of metabolism? Considering this information, also pertinent items of earlier discussion as to protein metabolism, tell why a nephritic diet is frequently restricted as to both protein and salt intake?

9. What two mechanisms operate at the kidneys to maintain the normal concentration of buffer salts in the blood? As a result, what salts would you expect to be eliminated in the larger than usual quantities (a) in acidosis, (b) in alkalosis?

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Valences of Elements and Radicals

Hydrogen	H^{+}

Metal elements

Potassium	K^{+}
Sodium	Na^{+}
Silver	Ag^{+}
Mercurous	Hg^{+}
Mercuric	Hg^{++}
Cuprous	Cu^{+}
Cupric	Cu^{++}
Barium	Ba^{++}
Calcium	Ca^{++}
Lead	Pb^{++}
Magnesium	Mg^{++}
Nickel	Ni^{++}
Zinc	Zn^{++}
Ferrous	Fe^{++}
Ferric	Fe^{+++}
Chromium	Cr^{+++}
Aluminium	Al^{+++}
Stannous	Sn^{++}
Stannic	Sn^{++++}

Metal acting radicals

Ammonium	NH_4^{+}
Methyl	CH_3^{+}
Ethyl	$C_2H_5^{+}$
Glyceryl	$C_3H_5^{+++}$

Oxygen	O^{--}
Hydroxyl	OH^{-}

Acid radicals

Chloride	Cl^{-}		
Bromide	Br^{-}		
Iodide	I^{-}		
Sulfide	S^{--}		
		Chlorite	ClO_2^{-}
Chlorate	ClO_3^{-}	Hypochlorite	ClO^{-}
		Perchlorate	ClO_4^{-}
Bromate	BrO_3^{-}	Bromite	BrO_2^{-}
Iodate	IO_3^{-}	Iodite	IO_2^{-}
Nitrate	NO_3^{-}	Nitrite	NO_2^{-}
Sulfate	SO_4^{--}	Sulfite	SO_3^{--}
Carbonate	CO_3^{--}		
Hydrogen carbonate	HCO_3^{-}		
Zincate	ZnO_2^{--}		
Stannate	SnO_2^{--}		
Phosphate	PO_4^{---}		
Monohydrogen phosphate	HPO_4^{--}		
Dihydrogen phosphate	$H_2PO_4^{-}$		
Aluminate	AlO_3^{---}		

Organic acid radicals

Acetate	$C_2H_3O_2^{-}$
Palmitate	$C_{15}H_{31}CO_2^{-}$
Stearate	$C_{17}H_{35}CO_2^{-}$
Oleate	$C_{17}H_{33}CO_2^{-}$
Tartrate	$C_4H_4O_6^{--}$
Oxalate	$C_2O_4^{--}$